Contents

1 DLC and a-C:H films **3**

1.1 Introduction . . . 3

1.1.1 Kulisch99-book [?] . . . 3

1.1.2 DLC22 [?] . . . 3

1.1.3 hydrocarbons . . . 3

1.2 Overview about papers . . . 3

1.3 IR bands . . . 4

2 CN_x films **5**

2.1 related chem. compounds . . . 5

2.1.1 Urotropine . . . 5

2.1.2 pyridine . . . 5

2.1.3 polyacronitrile . . . 5

2.2 nanotubes . . . 6

2.2.1 Lai03 . . . 6

2.2.2 Chen01 . . . 6

2.2.3 Hammer01 . . . 7

2.2.4 Ref. 17 in Hammer01 - **sehnat!** . . . 7

2.2.5 Marton94 . . . 8

2.3 FTIR and XPS . . . 8

2.3.1 Mutsukura99, TSF, cn/mutsukura99.pdf . . . 8

2.3.2 Jelínek00, TSF . . . 9

3 Si-related compound **11**

3.1 Analysis of silicones, chapter 10 (FTIR), D. R. Anderson . . . 11

3.1.1 Si-H . . . 11

4 Si-nitrides, carbides and carbonitrides **13**

4.1 About effort in Si-C-N compounds . . . 13

4.1.1 si-based_hard/sicn/Smirnova03 [?] . . . 13

4.1.2 si-based_hard/sicn/Peng01 Peng01 . . . 13

4.2 FTIR of silicon nitrides . . . 13

4.2.1 book - Silicon Nitride in Elecronics, V. I. Belyi et al., Elsevier 1988 [?] . . . 13

4.2.2 si-based_hard/sin/lucovsky83 [?] . . . 14

4.2.3 si-based_hard/sin/tsu86 [?] . . . 14

4.2.4 ftir/lanford78 [?] . . . 14

4.2.5 Materials Science of Carbides, Nitrides and Borides, ed. Y.G. Gogotsi, R.A. Andrievski, NATO Science Series Vol. 68 . . . 14

4.2.6 si-based_hard/sin/lattemann03 [?] . . . 14

4.2.7 si-based_hard/sin/parson91 [?] . . . 15

4.3 FTIR on Si-C-N films . . . 15

4.3.1 papers1/si-based_hard/sicn/peng01 [?] . . . 15

4.4 FTIR on Cl-related films . . . 15

4.4.1 ftir/Cl-related/Upadhyay04 [?] . . . 15

5 Organosiloxanes **17**
5.1 Overview about papers . . . 17
5.2 Results on plasma deposition from HMDSO . . . 18
5.2.1 VanOoij97-HMDSO4 [?] . . . 18
5.2.2 Alexander96-HMDSO7 [?] . . . 18
5.2.3 Alexander97a-HMDSO10 [?] . . . 18
5.2.4 Tien72-HMDSO11 [?] . . . 19
5.2.5 chybi!-HMDSO14 [?] . . . 19
5.2.6 Aumaille00-HMDSO19 [?] . . . 19
5.2.7 Ito-HMDSO20 [?] . . . 19
5.2.8 Poll93-HMDSO21 [?] . . . 20
5.2.9 Lamendola97-HMDSO16 [?] . . . 20
5.2.10 Vallee97 [?] . . . 20
5.3 Application of HMDSO films . . . 20

6 Organosilazanes **21**
6.1 Overview of FTIR and XPS on HMDSN . . . 21
6.1.1 Seekamp00 (paper3/hmdsn) . . . 21
6.1.2 Baraton98 (paper3/hmdsn) . . . 21
6.1.3 Pecheur99 (paper3/hmdsn) . . . 21
6.1.4 Fainer03 /papers/hmdsn . . . 22
6.1.5 Gengenbach99 /papers3/hmdsn . . . 22
6.1.6 Grafting with HMDSN - citation? . . . 23
6.1.7 Ungureanu03 (papers3/hmdsn) . . . 23
6.1.8 Tanaka98 . . . 23
6.1.9 Fainer03 (papers/hmdsn) . . . 23

7 XPS - summary **25**
7.1 CN_x films . . . 25
7.2 Summary tables . . . 25
7.3 My fit of XPS on HMDSO and HMDSN APG films . . . 29

8 Infrared absorption - summary **31**
8.1 Good papers specific to FTIR . . . 31
8.2 Summary tables . . . 31

Bibliography **37**

Chapter 1

DLC and a-C:H films

1.1 Introduction

1.1.1 Kulisch99-book [?]

Carbon can exist in a vast variety of crystalline and, especially, amorphous modifications. The most important crystalline phases are diamond and graphite that are classical examples of sp^3 and sp^2-bonded carbon materials, respectively. In contrast to the tetrahedral sp^3-bonded diamond, the sp^2-bonded graphite has no analog with the other elements of group IV (Si, Ge and Sn) [?], [?]. The reason can be found in the electronic structure of the core of the elements of the first?? row of the periodic table [?], which consists of s-electrons only and contains no p-electrons. Any p-electrons in the core have a repulsive effect on p-valence electrons, forcing them into bonds with neighboring atoms [?]. This means that sp^2 hybridization takes place only for elements of the first row. The ability to form double and triple bonds, however, is (besides the ability to form long chains and cyclic compounds) responsible for the immense variety of organic chemistry.

The number of possible amorphous carbon films, considering the nature of bonding, composition and structure, is very high. This is especially true if the consideration also includes hydrogen containing films and if, in addition, classical polymers such as polyacetylene $(\text{-CH-})_n$ and polyethylene $(\text{-CH}_2\text{-})_n$ are taken into account. This variety of possible structures corresponds to a extreme variation of film properties, which ranges from soft to superhard. A classification of the various types of (hydro)carbon layer can be performed through their hydrogen content, on the one hand, and their density [?] or the fraction of sp^3 bonds, on the other hand.

1.1.2 DLC22 [?]

DLC films contain both the tetrahedral C-C bonding configuration (sp^3), as in diamond, and trigonal bonding configuration (sp^2), as in graphite. Depending on the relative fractions of the sp^3 and sp^2 contents in DLC, the properties of the hardness, optical transparency, smoothness, and chemical inertness vary over a wide range. Therefore, the determination of the sp^3/sp^2 ratio is a very important issue in characterizing carbon films. The characteristic bonding configuration of hydrogenated DLC films have been studied using infrared spectroscopy [?],

1.1.3 hydrocarbons

methane CH_4, ethane C_2H_6, ethylene C_2H_4, acetylene C_2H_2

1.2 Overview about papers

acetylene: DLC5
theory of bonds: DLC7
bandgap: DLC10
IR spectra: DLC1, DLC4, DLC5

1.3 IR bands

band No.	configuration	predicted freq. [cm^{-1}]	observed freq. [cm^{-1}]	observed FWHM [cm^{-1}]
1	sp^1CH	3305	3300	44
2	sp^2CH (arom.)	3050	3045	68
3a	sp^2CH_2(olef.)	3020	-	-
4	sp^2CH(olef.)	3000	3000	78
5a	sp^3CH_3(asym.)	2960	-	-
3s	sp^2CH_2(olef.)	2950	-	-
6a	sp^3CH_2(asym.)	2925	2920	?
7	sp^3CH	2915	2920	88
5s	sp^3CH_3(sym.)	2870	-	-
6s	sp^3CH_2(sym.)	2855	2850	78

Table 1.1: C-H stretch absorption bands [DLC4]. Predicted are taken from [2], [3]. Di- and trihydrogen bands are doublets with a "symmetric" (s) and "antisymetric" (a) vibration.

Determination of the absorption coefficient and the optical band gap is based on transmittion and reflection spectra [1]. Deposition of films described in [?], [4]. The bonding type (sp^3, sp^2 and sp^1) can be determined by the spectroscopy of the infrared vibrations of CH, CH_2 and CH_3 groups.

Chapter 2

CN_X films

2.1 related chem. compounds

2.1.1 Urotropine

Urotropine ($C_6H_{12}N_4$) also called hexamethylenetetraamine (HMTA) contains the nitrogen and carbon atoms in positions closely resembling those in the predicted β-C_3N_4. The difference between this molecule and a subnanometer size crystallite of β-C_3N_4 is mainly that carbon dangling bonds are hydrogen terminated, altough the nitrogen atoms in urotropine are in tretrahedral, rather than trigonal sites. [Marton94]

Note, in XPS of urotropine C1s should be composed from two peaks C-H and C- N (sp^3). Nobody gives both positions!

Table 2.1: FTIR active modes based on theoretical calculations in [1]

wavenumber [cm^{-1}] experimental	wavenumber [cm^{-1}] theoretical	bonds
2955	2960	C-H stretch
2919	2914	C-H stretch
1456	1458	CH_2 scissors
1370	1368	CH_2 wag
1240	1243	CH_2 rock
1007	1009	N-C stretch
812	825	N-C stretch
673	677	N-C-N bend
512	504	N-C-N wag

Chen01: For urotropine [21 and 22], the C 1s binding energy is 286.9 eV and N 1s is 399.4 eV.

References:

1) Vibrational frequencies and structural determinations of hexamethylenetetraamine, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 58, Issue 7, May 2002, Pages 1347-1364 James O. Jensen =¿ papers1/cn/related_struct/jensen02.pdf

21) D. Marton, K.J. Boyd, A.H. Al-bayati, S.S. Todorov and J.W. Rabalais. Phys. Rev. Lett. 73 (1994), p. 118.

22) Mansour and S. Ugolini. Phy. Rev. B 47 (1993), p. 10201.

2.1.2 pyridine

Chen01: For pyridine [21 and 22], the carbon binding energy is 285.5 eV

21) D. Marton, K.J. Boyd, A.H. Al-bayati, S.S. Todorov and J.W. Rabalais. Phys. Rev. Lett. 73 (1994), p. 118.

22) Mansour and S. Ugolini. Phy. Rev. B 47 (1993), p. 10201.

2.1.3 polyacronitrile

polyacronitrile (C 1s binding energy: 286.4 eV and N 1s binding energy: 399.6 eV) [Cheng01]

2.2 nanotubes

2.2.1 Lai03

1) The crystalline properties of carbon nitride nanotubes synthesized by electron cyclotron resonance plasma, Thin Solid Films, Volume 444, Issues 1-2, 1 November 2003, Pages 38-43 S. H. Lai, Y. L. Chen, L. H. Chan, Y. M. Pan, X. W. Liu and H. C. Shih =¿ papers3/nanotubes/cn_nanotubes/lai03.pdf

FTIR - The absorption band between 1250 and 1750 cm^{-1} shows strong evidence for the incorporation of nitrogen into the carbon network,which induced the FTIR active G and D bands [15] .This very broad absorption band is resulted from the superimposition of the NH and CH bending vibrations [16] .The absorption features at 2256 cm and 2926 cm are corresponding to C≡N stretching vibrations and CH stretching vibra- tions,respectively.The band at 3451 cm corresponds y 1 to OH in adsorbed H_2O from atmosphere on the surface dark layer and the peak is substantially reduced after polishing the surface.A relatively weak absorption peak at 2341 cm^{-1} was observed after the surface dark layer being removed,as shown in Fig.3b,which is probably due to the C=O vibration w 17 x resulting from the substitution of oxygen for carbon in the CN-NTs.

XPS - The C (1s)line (Fig.5a) was deconvoluted into two peaks at 287.4 and 286.3 eV,which are consistent with Marton et al. [18] and our previous results [14] .By the theoretical calculations [19] ,the substitution of oxygen atom is minor and does not alter the binding energy and the global structure of the tube,so we do not take the oxygen effect into account.The binding energy of the carbon shifts towards higher position with the binding to nitrogen because of the decreasing electron density on the carbon atoms, which is due to the smaller electronegativity of C ($\chi = 2.5$)than N ($chi = 3.0$).The free carbon peak at 284.5 eV was neglected because the front dark layer of the composite membrane was polished away.By comparing with urotropine ($C_6H_12N_4$,sp^3 binding energy:286.9 eV) [20] and pyridine (C_5H_5N,sp^2 binding energy: 285.5 eV) [21],the carbon peak at 287.4 eV and 286.3 eV are assigned to be sp^3 and sp^2 bonding,respectively.

N (1s)line (Fig.5b)was deconvoluted into two peaks at 401.7 and 400.3 eV in accordance with Marton et al. [18] and our previous results [15]. By using the same analogy for the carbon peaks,the nitrogen peaks at 401.7 eV and 400.3 eV are assumed to represent the sp^2 and sp^3 bondings,respectively.Casanovas et al. reported that highly coordinated N atoms replace C atoms in the graphene sheets (401 -403 eV)and pyri- dinic N (399 eV)w 22 x .The ratios of N y C are 0.78 and

References:

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2.2.2 Chen01

The characterization of amorphous carbon nitride films grown by RFCVD method, Journal of Non-Crystalline Solids, Volume 283, Issues 1-3, May 2001, Pages 95-100 Sheng-Yuan Chen and Juh-Tzeng Lue

XPS - As shown in Fig. 3(a), the carbon 1s line was decomposed into three components occurring at 284.6, 285.5 and 288.3 eV. The 284.6 eV peak corresponds to the existence of nano-crystalline graphite [14 and 20]. The results of Raman spectra also reveal the graphite-phase at 1580 cm-1. In general, the XPS spectra of -C3N4 are compared with pyridine C5H5N and urotropine C6H12N4. For pyridine [21 and 22], the carbon binding energy at 285.5 eV has the same value as the C 1s signal occurring in this experiment. For urotropine [21 and 22], the C 1s binding energy is 286.9 eV and N 1s is 399.4 eV. The trigonal structure of -C3N4 has a higher binding energy of CN bonds rather than the tetrahedral urotropine. In these measured XPS spectra, the C 1s at 288.3 eV and N 1s at 398.5 eV are referred to the structure of urotropine. The peaks at 285.5 and 288.9 eV thus indicate two different binding states for carbon with nitrogen (21). The corresponding nitrogen binding energy is at 399.7 and 398.5 eV. The additional peak at 405 eV was identified to be due to N-O bonds.

FTIR - The peak at 2352 cm^{-1} of the FTIR spectra as shown in Fig. 4 is caused by the absorption of CO2 molecules existing in the ambient air. Unfortunately the CN stretching mode occurring at 2200 cm-1 is not seen for the low concentration of the nitrogen doping below 9%. The intensity of lines near 1570 cm^{-1} for the sp2 bonds becomes active with increasing the NH4OH concentration. Carbon-carbon stretching vibrations in aromatic groups near 1550 cm^{-1} become IR active due to the addition of nitrogen

at neighboring sites. The absorption peaks instead of the transmission dips were tested for the uppermost curve. Fig. 5 shows the Raman spectra of a-CN:H compared with a-C:H. Both are decomposed into graphitic G at 1575 cm^{-1} and disorder D band at 1360 cm^{-1} as shown in Fig. 5, respectively. The symmetric E2g Raman- active G band for graphite is broken dramatically as the NH4OH partial pressure increases (19). The intensity ratio ID/IG increases as the incorporated nitrogen content increases. It is accompanied by a slight reduction of the FWHM of G band from 132-117 cm^{-1}. These results show that the increase of the nitrogen content in a-C:H films induces an increase of sp2 fraction and the grain size of graphite microcrystallines in the films [30 and 31].
References:
(21) D. Marton, K.J. Boyd, A.H. Al-bayati, S.S. Todorov and J.W. Rabalais. Phys. Rev. Lett. 73 (1994), p. 118.
(22) Mansour and S. Ugolini. Phy. Rev. B 47 (1993), p. 10201.

2.2.3 Hammer01

CN_x films The binding energies found are 398.3 eV (A1), 400.4 eV (A2) and a small peak at 402.4 eV (A3). The width (FWHM) of all subpeaks is 1.9 eV. It is generally accepted that the A2 component is due to substitutional N in extended graphitic structures. (*my comment: C=N, according to Marton94*) Theoretical calculations suggest that with increasing size of these clusters the binding energy (EB) shifts to higher values (401 eV) (12). The FWHM is determined by their size-distribution. This graphitization effect was detected for samples grown at elevated temperatures (¿350C) [13 and 14]. The most contradictory peak assignment in the literature refers to the component A1. Most authors attribute this peak to N atoms bonded to sp3 hybridized carbon [4, 8, 12, 15 and 16], while others identify A1 exclusively, due to pyridine like structures at the edges of graphitic clusters [17, 18 and 19] or as caused by nitrile (CN) groups [20]. None of these suggestions is very satisfactory to explain our spectra. In the first case one has to assume for N rich samples a high fraction of sp3 carbon or a preferential bonding of N with sp3 C, both situations are not very probable. The second assignment would indicate an entirely aromatic nature of the material. In the later case, Snis et al. concluded from the comparison of the Raman activity with graphitic modes that the contribution of the CN groups, observed as a small peak at 2200 cm-1, has only a minor effect on the XPS spectra [17]. We propose a multi-structural nature of A1 and assign as the main contribution to non-aromatic CN bonds with N having an sp3 hybridization character similar to that in the NH3 molecule. Furthermore, also N bonded to sp3 C (NC3) and for N rich samples nitrile as well as aliphatic groups (NC2) contribute to A1. Only a small effect on the spectra is expected from the pyridine structure (aromatic NC2) with a calculated position at 399.2 eV (12). Finally, the small A3 component at 402.4 eV results from trapped N2 molecules in the film [3 and 12]. The commonly used identification of A3 as due to N-O groups can be excluded in our in situ XPS diagnosis. The deconvoluted C 1s core-level spectra, shown in Fig. 3, include the spectrum of a a-C film grown without nitrogen ion beam assistance. The C 1s peak position of the a-C film located at 284.3 eV is identified as due to graphitic structures [15]. Most authors attribute the minor component at 285.3 eV to sp3 carbon [15 and 21]. The inclusion of an increasing amount of N causes a systematical widening and shifting of the C 1s spectrum to higher binding energies. This effect is caused by the formation of a variety of different CN binding environments, contributing to the high energy side of the spectrum and the reduced number of pure graphitic sites at 284.3 eV (B1). Three new components can be fitted at 285.2 eV (B2), 286.2 eV (B3) and 287.4 eV (B4), all with a FWHM=1.6 eV. According to Hammer et al. [3], the components can be assigned to the following structures: the B2 peak is attributed to the aromatic C3N configurations, B3 is assigned to the non-aromatic C3N phase, including sp3 C bonded to N (C4N) and B4 represents the non-aromatic C2N2 configuration. From Fig. 3 it can be easily seen that the intensity ratio of non-aromatic to aromatic structures, (B3+B4)/(B2), increases with the addition of N. Similar behavior of the ratio A1/A2 can be observed in the N1s spectra (Fig. 2).

and much more for CN_x:H in the paper!!

2.2.4 Ref. 17 in Hammer01 - sehnat!

17. A. Snis, S.F. Matar, O. Plashkevych and H. Agren J. Chem. Phys. 111 (1999), p. 9678 Core ionization energies of carbon-nitrogen molecules and solids A. Snis and S. F. Matar Institut de Chimie de la Matiere Condense de Bordeaux, CNRS, 87, Avenue du Dr. Albert Schweitzer, 33608 Pessac, France O. Plashkevych and H. Agren Department of Theoretical Chemistry, Royal Institute of Technology, S-100 44, Stockholm, Sweden (Received 27 April 1999; accepted 9 September 1999)

Core ionization energies have been calculated for various carbon- nitrogen molecules and solids. The systems investigated contain many of the bonding possibilities which presumably arise in carbon nitride

thin films prepared under varying conditions. The molecular core ionization energies are calculated by the SCF self-consistent field method. Several singly, doubly, and triply bonded CxNyHz species have been considered. Core ionization energies of two C11N4 C sp2 and C sp3solids have been calculated with the full-potential linearized augmented plane wave method. Molecular C 1s binding energies increase with approximately 1 eV for each singly or doubly bonded nitrogen atom attached. The trend is similar in the solids although variations and saturation effects are obtained due to hybridization and nitrogen content. The 1s binding energies of two-coordinated nitrogen atoms in C sp2 molecules and of pyramidal three-coordinated nitrogen atoms in C sp3 molecules are close to each other. The differences depend on the size of the systems and the number of CH3 groups attached. In the solid state compounds, where no CH3 groups are present, the energies of two-coordinated nitrogen in a C sp2 environment are always lower than the energy of pyramidal three- coordinated nitrogen in the C sp3 solid, by more than 1 eV. Concerning the micro structure in thin CNx films, comparisons of the computational results with experiment indicate that at low nitrogen concentrations the atomic configuration close to the N atoms are mostly of sp3 character. At higher N contents more two-coordinated nitrogen atoms are incorporated. The N 1s binding energy shifts observed at high substrate temperatures could be explained by either a gradual formation of three-coordinated N atoms in a graphitic-like C sp2 environment or by local domains containing high N concentrations. (c)1999 American Institute of Physics.

2.2.5 Marton94

- only as a printed paper Carbon Nitride Deposited Using Energetic Species: A Two-Phase System D. Marton, K. J. Boyd, A. H. Al-Bayati, S. S. Todorov, and J. W. Rabalais Department of Chemistry, University of Houston, Houston, Texas 77204-5641 Phys. Rev. Lett. 73, 118-121 (1994) Carbon nitride films deposited by three different methods have been analyzed using in situ Auger electron spectroscopy and ex situ x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry. The XPS data for all 27 samples indicate that these films have a similar composition consisting of two phases. One phase has a stoichiometry near C3N4 and is identified as a tetrahedral component. The other phase has a variable stoichiometry from C5N to C2N and is identified as predominantly an sp2 bonded structure. For a film composition of [N]/[C] ¡ 1, the tetrahedrally bonded component grows only moderately as the nitrogen content of the films is increased. (c)1994 The American Physical Society URL: http://link.aps.org/abstract/PRL/v73/p118

2.3 FTIR and XPS

2.3.1 Mutsukura99, TSF, cn/mutsukura99.pdf

CN_x films obtained (PECVD CH_4/N_2) were polymer-like transparent soft films. The IR spectra indicate five absorption bands at 3200-3500 cm^{-1}, 2800-3000 cm^{-1}, 2100-2250 cm^{-1}, 1500-1800 cm^{-1} and 1300-1500 cm^{-1} regions.

The 3200-3500 cm^{-1} band is composed from three absorption peaks at 3200, 3300 and 3450 cm^{-1} which were decided by the Gaussian fitting and were consistent with the reported [2] and predicted values [13]. They are identified with N-H stretching vibration, and are associated with both ¿NH and NH_2 components.

The 1500–1800 cm^{-1} band is predicted to contain some absorption modes such as double bonded C=C and C=N stretching and N-H bending modes.

The absorption band at 2800–3000 cm^{-1} is identified with C-H stretching vibration, which is normally observed in diamond-like carbon films [14].

The absorption band at 1300–1500 cm^{-1} region has been reported to be related with C-H [2] and C-N [12] bonds.

As to the absorption band at 2100–2250 cm^{-1}, the contribution of C≡N triple bond has been reported until now [2,3,5-12]. In these previous reports a broad absorption band having single absorption peak has been observed for almost all of the carbon nitride films, except the samples reported by Kaufman et al. [5] which indicated two absorption peaks at 2130 and 2200 cm-1. However, for our samples the band contains obviously several components: 2105, 2160, 2190, 2215 and 2245 cm^{-1}. The vibration frequencies of the C≡N stretching modes associated with both nitrile (-C≡N) and isonitrile (-N≡C) structures, greatly depend on a type of component bonded to these structures. Those appear at 2245-2255 cm^{-1} and 2226-2229 cm^{-1} for the nitrile, and at 2146-2183 cm^{-1} and 2122-2125 cm^{-1} for isonitrile, when they are bonded to hydrocarbons and aromatic rings, respectively.

Table 2.2: Bonding energies

bond	energy [kcal/mol]
C-N	69.7
C=N	147
C≡N	207

2.3.2 Jelínek00, TSF

XPS analyses
The N1s spectral lines displayed in Fig. were found to be broad (2.8 eV) suggesting more bonding states of nitrogen atoms. Reasonable fits were obtained with three Gaussian functions 1.5 eV wide (FWHM) peaked at 398.8±0.1 (sp^3C-N), 399.9±0.2 (N-H) and 400.9±0.2 eV (sp^2C-N).

FTIR spectra
Nitrile, isonitrile and carbodiimide are assumed to play imporatnt role in of the bridges between aromatic carbon clusters [33,37]. *Position of isonitrile does not agree with Mutsukura99 above*

Table 2.3: FTIR identification

wavenumber [cm-1]	bonds
1600-1630	C=C, C=N, N-H, O-H
3300	N-H, O-H
2220-2230 cm-1	-C≡N nitrile
2115-2175 cm-1	-N≡C isonitrile
2105-2155 cm-1	-N=C=N- carbodiimide

Chapter 3

Si-related compound

3.1 Analysis of silicones, chapter 10 (FTIR), D. R. Anderson

3.1.1 Si-H

- Si-H stretching vibration is one of the most characteristic infrared frequencies for organosilicon materials. It gives a strong band in the 2100 to 2300 cm^{-1} region where there is very little interference from other bands. It has been shown that the position of the Si-H stretching frequency is dependent on the inductive power of the other groups on the silicon atom, the more electron-withdrawing groups causing shifts to higher frequencies [57].

  The position of the Si-H streching band for a particular compound can be predicted from a table of constants characteristic of each substituent [?]

group	E [cm^{-1}]	group	E [cm^{-1}]
F-	760.8*	Me_2N-	715.5*
Cl-	752.8	CH_2 =CH-	709.2
MeO-	734.4*	CH_3-	705.9
EtO-	732.0*	Et-	699.1
H-	724.8	Me_3SiCH_2-	687.6
HO-	718.6*	Me_3Si-	684.8

Chapter 4

Si-nitrides, carbides and carbonitrides

4.1 About effort in Si-C-N compounds

4.1.1 si-based_hard/sicn/Smirnova03 [?]

Silicon carbonitride thin films are attractive since they are expected to combine the properties of silicon nitride and the hypothetical carbon nitride. These films would be resistant to high temperatures and corrosive environments. They may be used as variable band gap materials, dielectric layers, diffusion barriers in semiconductor technology and the materials having unique tribological behaviour.Ternary Si -C -N compounds were commonly deposited using CVD techniques at elevated temperatures [1-3]. Low-temperature deposition processes are preferred for practical application in order to make electronic devices and protective coatings.However, only a few attempts to prepare SiCN alloys have been carried out at low growth temperatures primarily using physical vapour deposition (PVD) methods [4 -10] .

In depositing films with CVD process mixtures of CH_4, N_2, H_2 and SiH_4 (5% SiH on N dilution) gases in various proportions are widely used as basic reagents [8,11,12] .Such gas mixtures are hazardous.Therefore, the search for novel new volatile precursors to fabricate silicon carbonitride films is required. However,there is no great variety of such volatile substances. Organosilicon compounds could be used as single- source precursors containing silicon, nitrogen, and carbon.Being of no hazard,they are particularly promising for $Si_xC_yN_z$film deposition.

4.1.2 si-based_hard/sicn/Peng01 Peng01

Silicon carbide nitride material is a covalently cross-bonded ternary system with short-range order, which posses the excellent mechanical, chemical, electrical and optical properties of silicon carbide and silicon nitride [1]. Especially, amorphous silicon carbide nitride thin (r)lms (a-SiCx Ny) have recently been attracting much attention for its apparent tunability over a wide range from the band gap of SiC (2.86 eV) to insulating film of Si3 N4 ($\approx$ 5.0 eV) by controlling the composition, which are of interest in integrated circuits, optical device fabrication and material surface protection [2]. However, only a few efforts have been spent in the recent years to synthesis Si-C-N thin films by reactive sputtering a silicon carbide target in N2+Ar atmosphere [3], nitrogen-ion implantation into SiC [4] (microwave) plasma-assisted or electron cyclotron resonance chemical-vapor-deposition (PACVD, MWCVD or ECR-CVD) using SiH4 -NH3 -CH4 [5,6] or laser ablation of a SiC target in nitrogen atmosphere [7]. Chen et al. [6] reported a SiCx Ny thin film, which contains N 574.4 eV using ECR-CVD. In our data, there is no report on synthesis of SiCx Ny (r)lms by rf reactive sputtering a Si3 N4 target in methane and argon atmosphere.

4.2 FTIR of silicon nitrides

4.2.1 book - Silicon Nitride in Elecronics, V. I. Belyi et al., Elsevier 1988 [?]

p. 105 The IR absorption spectrum of partly and completely crystallized silicon nitride reveals the bands typical of the crystalline α-Si_3N_4 phase: 830–835 cm^{-1}, 870–880 cm^{-1} (the two strongest bands), 920 cm^{-1}, 1015-1020 cm^{-1} (weak bands). All the vibrations are valence ones.

p. 85 Valence and deformation vibrations of all main oscillators of Si_3N_4 occur in the interval of wavelengths entering the IR range (Si-N: 11.6-12.0 μm, i.e. 862–833 cm^{-1} - valence [45], N-H: 3.0 μm, i.e. 3333 cm1 - valence, 6.4 μm, i.e. 1563 cm^{-1} - deformation [46], Si-NH- Si: 8.6 μm, i.e. 1163 cm^{-1} - valence [46], Si-H: 4.7 μm, i.e. 2128 cm^{-1} - valence [46], 8.4 μm, i.e. 1190 cm^{-1} - deformation [35]).

4.2.2 si-based_hard/sin/lucovsky83 [?]

title: Nitrogen-bonding environments in glow-discharge-deposited a-Si:H films

- a-Si:H films - 2000 cm1 stretching of Si-H, 630 cm1 bending (or wagging) of Si-H
- a-SiN:H films - 2060 cm1 Si-H, 840 cm^{-1} in-plane Si-N stretching mode, 3350 cm1 N-H stretching vibration, 1150 cm1 N-H bending vibration

4.2.3 si-based_hard/sin/tsu86 [?]

title: Silicon nitride and silicon diimide grown by remote plasma enhanced chemical vapor deposition *Are the films amourphous? Probably.*
Films were grown by remote PECVD from mixture of SiH_4 or Si_2H_6 with NH_3 or N_2/He. We have found that films grown from N_2 and deposited at subst. temperature in excess of 350°C have a composition corresponding to stoichiometric Si_3N_4, whereas films deposited from NH_3 require subst. temperature in excess of about 500°C to eliminate bonded H and yield the same stoichiometric composition. In contrast films grown from NH_3 at temperatures in the range of 50 to 100 ^circC have a chemical composition corresponding to silicon diimide, $Si(NH)_2$. Films grown from NH_3 at intermediate substrate temperatures are solid solutions of Si_3N_4 and $Si(NH)_2$.

- Si_3N_4 films deposited from SiH_4+N_2: SiH stretching vibration 2180 cm^{-1} (diminished for $T >$ 350°C), SiN vibration at 835 cm^{-1}, silicon (Si-Si) breathing at about 470 cm^{-1}
- SiNH films deposited from SiH_4+NH_3: NH stretching vibration centered at about 3335 cm^{-1} (medium ir activity), NH bending vibration at 1175 cm^{-1} (strong ir activity), SiN stretching vibration whose frequency varies between 885 and 835 cm^{-1}, silicon breathing vibration whose frequency varies between 430 and 490 cm^{-1}. In addition the films with high concentration of NH groups display a shoulder on the high frequency side of the 3335 cm^{-1} band and an additional weak feature at 1545 cm^{-1}. They are interpreted as NH_2 stretching vibration and a NH_2 scissors bending vibration, respectively.

4.2.4 ftir/lanford78 [?]

title: The hydrogen content of plasma-deposited silicon nitride
Sensitivity factors for SiH and NH - IR bands, 3350 and 2160 cm^{-1}, are necessary to estimate the concentrations of these groups in the SiN:H films. The factors were obtained from comparison of nuclear resonant reaction analyses (NRRA) that determined H content and IR absorption. Total amount of H atoms/cm^2 from NRRA can be compared with area under absorption peak.

SiO_2 films deposited for comparison did not exhibit any SiH groups but OH bands, 3645 cm^{-1} (probably isolated OH) and 3390 cm^{-1} (probably water).

4.2.5 Materials Science of Carbides, Nitrides and Borides, ed. Y.G. Gogotsi, R.A. Andrievski, NATO Science Series Vol. 68

(p. 96) broad and complex band centered at 3355 cm^{-1} assigned to Si-NH-Si imido and Si-NH_2 amido surface groups [28,29]

4.2.6 si-based_hard/sin/lattemann03 [?]

- Si_3N_4 films: 875–896 cm^{-1} asymmetric in plane Si-N stretaching vibration mode [7]. It is well known that the oxygen incorporation in silicon nitride causes a shift in the absorption band due to Si-N bond stretching near 880 cm towards higher wavenumbers.The large value of the full width at half maxima (FWHM)of this band is consistent with the previously reported data [7,17] and refers to the amorphous nature of Si_3N_{4-x} films.The small peak absorption band observed at 490 cm^{-1} corresponds to Si-N breathing mode [17] .It can be noted that the samples do not have

a characteristic absorption band at 1040 cm^{-1} of the asymmetric stretch mode of the Si-O-Si bond.This proves that there is no significant amount of silicon dioxide in the samples.

7. G. Parsons, J.H. Souk and J. Batey. J. Appl. Phys. 70 (1991), pp. 1553- 1560.
17. T. Serikawa and A. Okamoto. J. Electrochem. Soc. 131 12 (1984), pp. 2928-2933.

4.2.7 si-based_hard/sin/parson91 [?]

title:
There is a large amount of literature dealing with the vibrational frequencies associated with Si-H, N-H and Si-N bonding groups. The assignments for these modes in PECVD silicon nitride are given in Ref. 5 and are briefly summarized here: (1) N-H stretching mode at 3330 cm^{-1} , (2) Si-H stretching at 2140 cm^{-1} , (3) N-H2 scissors at 1550 cm^{-1}, (4) N- H and N-H_2 bending at 1150 cm^{-1}, (5) Si-N stretching between 870 and 820 cm^{-1}, and (6) the Si-N "breathing" mode between 430 and 490 cm^{-1}. The sharp absorption feature occasionally observed at 1100 cm^{-1} is related to incomplete subtraction of a Si-0 related feature in the silicon

4.3 FTIR on Si-C-N films

4.3.1 papers1/si-based_hard/sicn/peng01 [?]

title:
Xiao et al. [3] and Savall et al. [11] pointed that although each of its absorption band could be traced to a certain binary bond, the exact vibration frequency was slightly different owing to the complex chemical bonding surrounding each element. For example, the peak at 460 and 1000 cm^{-1} [12] can correspond to asymmetric and symmetric stretching vibration of Si-N bond. Several Si-C stretching mode were observed corresponding to wave numbers 610, 800-823 cm^{-1}. A weak C-N bond at 1100 cm^{-1} [12] can also be fitted in all four spectra. A broaden peak at 1250-1560 cm^{-1} corresponding to C-N, C=N and C=C bond and an additional weak peak at 2170 cm^{-1} corresponding to C≡N stretching mode can also be observed [4,13]. *They fitter broad peak 700–1200 cm^{-1} by three peaks: 800-822 cm1 Si-C, 996–1012 cm^{-1} Si-N and 1102–1112 cm^{-1} C-N.*

4.4 FTIR on Cl-related films

4.4.1 ftir/Cl-related/Upadhyay04 [?]

The untreated PVC copolymer shows two distinct C-Cl vibrations at 695 cm^{-1} (S'HH) and a more intense band at 613 cm^{-1} (S HH) [23 -25].Where, the S 'HH and S HH bands are,respectively,due to out-of-plane and in-plane C-CHCl-C skeletal modes trans to neighbouring hydrogen atom.

[papers1/ftir/Cl-related/Robinson95]: The Si-H vibrational frequencies for a series of chlorine-substituted silanes are 2118, 2168, 2213, and 2274 cm^{-1} , for $(CH_3)_3$Si-H, $(CH_3)_2$ClSi-H, $(CH_3)Cl_2$Si-H, Cl_3Si-H, respectively [34].

Chapter 5

Organosiloxanes

5.1 Overview about papers

- **VanOoij97-HMDSO4** Deposition from HMDSO (usually) in dc discharge on metal and plastic substrates.
  - film characterisation: weighting and calculation of thickness, i. e. deposition rate, expecting the density of 1.5 g/cm^3; FTIR using the reflection-absorption mode (RAIR) with Spectratech variable-angle specular reflection attachment (IR is well discussed!)
- **Alexander96-HMDSO7** Deposition from HMDSO and HMDSO/O_2 mixtures ($Q_{\rm hmdso}$ = 20 sccm, $Q_{\rm o2}$ =0–200sccm) in microwave discharge on Al substrates.
  - film characterisation: XPS (good described together with calibration and peak positions!)
- **Alexander97a-HMDSO10** Deposition from HMDSO/Ar and HMDSO/Ar/O_2 mixtures in microwave discharge on Al substrates.
  - application: corrosion protection
  - plasma diagnostics: mass spectroscopy of exhaust gases; utilization of parameters from Wagner's and Yasuda's work
  - film characterisation: IR absorption; XPS; water contact angle; resistivity agains corrosion
- **Tien72-HMDSO11** Deposition from HMDSO/Ar feed (0.3/0.1 Torr) in rf discharge on glass substrates.
  - application: in integrated optics, i. e. as a waveguide.
  - film charact.: refractive index, light scattering, electron micrographs
- **HMDSO14** model for polymerization of HMDSO, TENTO CLANEK CHYBI!!
- **Lamendola97-HMDSO16** Deposition from HMDSO and HMDSO/O_2 feeds (O_2/HMDSO= 0–20, p = 50–100 mTorr) in rf parallel plate discharge (2.0 and 4.0 W/cm^2) on Si substrates placed on third floating electrode.
  - application: list of references
  - plasma diagnostics: OES, actinometry
  - film charact.: XPS, FTIR, weighting
  - conclusions: explanation of deposition mechanismus for "high fragmentation" conditions (oxygen added into the feed)
- **Alexander97b-HMDSO17**
  - film characterisation: XPS only shortly
- **Aumaille00-HMDSO19** Deposition from HMDSO/O_2 and TEOS/O_2 feeds (fixed total flow rate at 16 sccm → change of monomer fraction) in helicon diffusion discharge on silicon? substrates.
  - plasma diagnostics: OES, actinometry

– film characterisation: spectroscopic ellipsometry; XPS; gravimetry and X-ray reflectivity; chemical etching using p-etch

- **Ito-HMDSO20** Deposition from HMDSO and TEOS with or without Ar and O_2 in ac and rf discharges (parallel plate).
  – film charact.: refractive index, dep. rate, XPS, contact angle
  – chybi citace a nenasla jsem ji ani INSPECem od r. 1996!

5.2 Results on plasma deposition from HMDSO

5.2.1 VanOoij97-HMDSO4 [?]

Films are divided into two groups:

- low power/high pressure (LW/HP) - There are better resolved peaks. A substantial amount of Si-CH_3 functionality seems to be retained and polymerization occurs partially in the chain-like structure.
- high power/low pressure (HW/LP) - Does not seem to be well defined. No long chains can be detected. There are fewer CH_3 groups and broader absorption bands indication a higher amount of crosslinking. It also displays a higher relative intensity of Si-H groups, which we interpret to be indicative of a higher monomer breakdown.

The XPS (no details presented) shows that the elemental composition of both the LW/HP and HW/LP films were approximately the same and also very close to that of pure PDMS (polydimethylsiloxane) indicating that the differences observed in FTIR spectra were the results of structural differences between the films. The TOF-SIMS results indicated that the LW/HP films had a structure which resembled that of the HMDSO monomer moce closely that that of the HW/LP films.

5.2.2 Alexander96-HMDSO7 [?]

Table 5.1: Results from XPS analyses in HMDSO7. HMDSO flow rate of 20 sccm

Q_{o2}	C	O	Si	C/O	C/Si	O/Si
0	50.31	22.89	26.80	2.12	1.88	0.85
10	39.93	32.33	27.74	1.24	1.44	1.17
20	35.57	35.56	28.88	1.00	1.23	1.23
40	29.94	41.43	28.63	0.72	1.05	1.45
100	22.66	47.57	29.77	0.48	0.76	1.60
200	18.74	50.76	30.50	0.37	0.61	1.66
HMDSO	66.67	11.11	22.22	6.0	3.0	0.5

5.2.3 Alexander97a-HMDSO10 [?]

From IR spectroscopy of films it could be supposed that a higher amount of O_2 is forcing demethylation of the films, changing bonds in the polymer from -H to -O-. A possible reason for these effects is a change in the neutral gas phase chemistry.It is known that the addition of O_2 to a reactive mixture of hydrocarbon fragments and H and H_2 can lead to high losses of methyl radicals because of the influence of O and OH radicals [HMDS010-13]. Simultaneously, the amount of atomic hydrogen will be reduced due to the production of water via OH radicals. If one adds small amounts of O_2 to a H_2/Ar plasma, an increase in atomic hydrogen and thus of hydrocarbon radicals may occur [HMDSO10-14]. This situation, however, is fas from our plasma conditions. Looking at the results from the mass spectrometry, no change in the amount of CH_4 in the gas phase, but an intensive H_2 and CO_2 production, was detected. It can be concluded from these circumstances that under certain conditions, H atoms tend to recombine among each other rather than to form $C_xH_yO_z$.

The relative proportion of the atoms at the polymer surface was found by XPS to be O/C/Si≈2.7/3/1 for pure HMDSO/Ar plasma and ≈2.7/0.3/1 for an additional oxygen admixture. HMDSO monomer has this ratio 0.5/3/1. It means that Si-O-Si cross-links prevail in films, which are grown in presence of additional oxygen.

5.2.4 Tien72-HMDSO11 [?]

A typical HMDSO film has a refractive index of 1.4880 at 632.8 nm (red He- Ne laser), 1.4960 at 514.5 nm (green argon laser) and 1.4996 at 488 nm (blue argon laser).

5.2.5 chybi!-HMDSO14 [?]

A simple model was deduced to describe the incorporation behavior of plasma polymerized films in terms of discharge power. The model was based on the dissociation of the chemical bonds of the monomer by inelastic collision with electrons in the plasma. The incorporation rate of the chemical bonds was given as a function of the discharge power under the assumption of the proportionality between the incorporation rate and the concentration of bonds in the plasma. The validity of the model was examined by measuring the relative incorporation rate of Si-O-Si and Si- CH_3 bonds in the films deposited by PECVD from HMDSO.

The incorporation rate of Si-O-Si bonds decreased with increasing discharge power. There exist a linear relationship between the reciprocal of the incorporation rate and the discharge power, which agrees well with the prediction of the model deduced for one dissociation process of Si-O-Si bond in HMDSO.

5.2.6 Aumaille00-HMDSO19 [?]

The influence of the organosilicon fraction (X_{org} = 5–100%) on the deposition rate and the refractive index of the deposited films at 1.96 eV (i. e. 633 nm) is reported.

It is clear that simple law between the deposition rate and the organosilicon fraction does not exist. At low values of X_{org}, low deposition rates of about 6–10 nm/min are obtained for both organosilicons. Upon adding the organosilicon precursor to oxygen, the deposition rate increases and saturates at 25 nm/min for the films deposited in pure TEOS plasmas and 50 nm/miin for the films deposited in pure HMDSO plasmas. Thus, at high values of X_{org}, the deposition rate is around two times large in HMDSO-derived films that in TEOS-derived films. This result is in agreement with what was found by Latreche [HMDSO19_22(PhD thesis)] and Sawada [?].

Ellipsometry in-situ $\Rightarrow$ If there are any voids they can be treated in Bruggeman effective medium aproximation (BEMA) as vacuum and not water vapours!

At a low X_{org}, the films are transparent in the 1.5–5 eV range, and their refractive index at 1.96 eV is very close to the one of a thermal oxide (n=1.46). The decrease of the refractive index as X_{org} is increased, indicates the presence of defects such as microporosity. The BEMA has been used to evaluate the fraction of voids, assuiming that the films is a homogeneous mixture of amorphous SiO_2 and voids [?]. The value of void fraction increase with X_{org} reaching 6% for the films deposited in 20%TEOS/80%O_2 plasmas, against 2% for the films elaborated by 20%HMDSO/80%O_2 plasmas. As X_{org} is above 30%, both the extinction coefficient and refractive index increase. For X_{org} =100%, the HMDSO-derived films are more absorbent in the UV (k(240nm) = 0.052) than TEOS-derived films (k(240nm) = 0.028). Moreover, at high values of X_{org} the organic films derived from HMDSO have a refractive index higher (n(633nm) $\approx$ 1.535) that the organic films derived from TEOS (n(633nm) $\approx$ 1.45).

For X_{org} <33%, the two elements detected are silicon and oxygen. Carbon is bellow detection limit of XPS analyses. Whatever the organosilicon, the O/Si content is close to two. ... discussion about position of Si 2p and O 1s peaks. By increasing the organosilicon fraction, the carbon content in the films increases very rapidly, whereas the oxygen and silicon contents decrease (Table 5.2).

Table 5.2: Results from XPS analyses in HMDSO19. Total flow rate of 16 sccm

	X_{org} =10%		X_{org} =100%	
	TEOS	HMDSO	TEOS	HMDSO
O(%)	67	68	34	34
Si(%)	33	32	13	24
C(%)	0	0	53	42

5.2.7 Ito-HMDSO20 [?]

With increasing input power, the refractive index increases monotonously (for pure monomer?). In case of HMDSO n_{600} = 1.39 for 20 W and n_{600} = 1.43 for 200 W. However, the composition found by XPS

does not change. Therefore they suppose that the increase is caused by increased density.

Table 5.3: Results from XPS analyses in HMDSO20. Pure monomer?

	TEOS	HMDSO
O(%)	53	27
Si(%)	37	32
C(%)	10	41

Decrease of refractive index with oxygen flow, for HMDSO from 1.42 (pure) to 1.39 (50sccm O_2). O/Si from 0.7 to 1.25 (40 sccm O_2). C/Si from 1.5 to 1.2.

Lower oxygen content in the SiO_x films results on higher refractive index [?]. Or higher carbon content increase the refractive index [?].

5.2.8 Poll93-HMDSO21 [?]

Exhaust gas spectrometry in the closed reactor and pure HMDSO $\Rightarrow$ according to the residence time in the reactor the stable gaseous products can be divided into four groups:

- mainly monomer (up to $\approx$ 20 s)
- mainly oligomers (20–110 s)
- mainly $Si(CH_3)_x$ (110–200 s)
- mainly C_xH_y and H_2 (200–310 s)

Compared with a flow reactor, our reactor is characterised by a high ration of buffer volume to active plasma region (about 100:1). The gas exchange plasma-buffer expands the time scale by diffusion and causes a decrease in deposition rate on the the discharge electrode.

In the first stage A (up to 180 s), the production of film-forming species from HMDSO leads to an increasing deposition rate, in spite of the decreasing HMDSO concentration. After consumption of the HMDSO and the stable silicon-containing reaction products the rate decreases (second and third stages, B and C) and reaches zero (at the end of C).

Refractive index increases along the transition from stage A to C. Beginning of deposition: 1.44, end of stage A: 1.49. Center of stage B: 1.52.

5.2.9 Lamendola97-HMDSO16 [?]

Given trend of composition of Si, O and C for various O_2/HMDSO ratios (podle pravitka to prepsat!).

5.2.10 Vallee97 [?]

Refractive index for HMDSO and TEOS and various discharges (40 kHz, Helicon, DECR) as function of monomer percentage in HMDSO/O_2 mixture. For pure HMDSO $n = 1.51$ for 40 kHz (density 1.25 g/cm^3) and $n = 1.59$ for DECR (density 1.35 g/cm^3). For pure HMDSO, DECR the IR spectrum is shown.

5.3 Application of HMDSO films

- **HMDSO11** application of HMDSO plasma polymerized films in integrated optics, i. e. as a waveguide. The films were deposited on the glass substrate. To serve as a light quide, the films must have a refractive index larger than that of the substrate.
- **HMDSO13** application of PP-HMDSO as corrosion protective coatings on metal substrates including carbon steel, stainless steel, Monel etc. Deposition in microwave large scale reactor (2.45 GHz). Resistance to simulated sea water (4% NaCl) was evaluated.
- **HMDSO9** Preparation of metal-organic films by co-deposition of metal with HMDSO (dc discharge).

Chapter 6

Organosilazanes

6.1 Overview of FTIR and XPS on HMDSN

6.1.1 Seekamp00 (paper3/hmdsn)

FTIR - There are six bands of similar amplitudes which give an insight into the bonding and growth processes for both materials. There is no band from Si-C and Si-N bonds in ceramic environments between 800 and 1000 cm^{-1} . The first two peaks at 790 and 840 cm^{-1} can be assigned to Si-$(CH_3)_2$ stretching vibrations and Si-$(CH_3)_3$ rocking vibrations respectively [6]. The Si-$(CH_3)_2$ absorption has a larger amplitude in samples made from HMDS while the Si-$(CH_3)_3$ absorption is of equal amplitude in both materials. This similarity means that there are more silicon atoms bound to species other than methyl with two of their bonds in samples made from HMDS compared to samples made from HMDSN. The Si-CH_3 deformation band at 1260 cm^{-1} [6] gives an indication of how many methyl groups there are in the samples. Hence there are more methyl groups bound to silicon in the sample made from HMDSN than in the sample made from HMDS. As there is no absorption for Si-CH_3 stretching vibrations at 775 cm^{-1} [6] detectable in samples from HMDSN and only a shoulder in material from HMDS, the excess methylgroups must be bound in Si-$(CH_3)_4$ configurations. The absorption of tetramethylsilane at 695 cm^{-1} [6] indicates the presence of this substance in the material but it is too small to be quantified. The absorption of in Si-CH_2-Si at 1240 cm^{-1} [6] has more than twice the amplitude for samples made from HMDS than for those made from HMDSN. A band at 1240 cm^{-1} is often interpreted as a Si-O-Si stretching vibration. For the materials discussed here such an assignment is not valid because of the absence of an Si-O-Si band around 430 cm^{-1} [6] that is always observed for oxidised films deposited under con- ditions discussed here [7,Seekamp98]. Two of the bands, the asymmetric Si-N-Si stretching vibration at 923 cm^{-1} [6] and the Si-NH-Si bending band at 1184 cm^{-1} , only appear in the spectra for material de- posited from HMDSN. Both these bands have almost the same amplitude in the spectrum of liquid HMDSN. Their relative amplitudes in the sample spectrum is similar to that found in the spectrum of liquid heptamethyldisilazane [9]. Hence the concentration of N-CH_3 bonds for the deposited material increased compared to the liquid starting material and the N-H bond is not fully preserved.

6.1.2 Baraton98 (paper3/hmdsn)

3320 cm^{-1} adsorbed water, 3780-3600 cm^{-1} ν(OH) stretching mode of different types of hydroxyl groups bonded to Ti atoms. The remaining bound water molecules are indicated by the broad band at 3480 cm^{-1} assigned to ν(OH) stretching mode in perturbed hydroxyl groups and by the band at 1620 cm^{-1} assigned to δ(OH) bending mode in water molecules. Bands centered at 2348 cm^{-1} assigned to CO_2, 1352 cm^{-1} to $\delta(CH_3)$ bending mode.

6.1.3 Pecheur99 (paper3/hmdsn)

SiO-H absorption at 3635 and 936 cm^{-1}, Si-H in O_2Si-H in the interval 2213-2236 cm^{-1}. Around 2966 cm^{-1} C- H_3 [13]. Two smaller bands between 1420-1350 cm^{-1} attributed to the deformation of SiC-H bond [14]. Moreover, IR spectra show an arear between 3390 to 3500 corresponding to N-H and N-H_2 vibration mode [15] and at 888 cm^{-1} to Si-NO.

13. J.H. Lee, Y.H. Lee and B. Farouk. J. Vac. Sci. Technol. A 14 5 (1996), 1p. 2702. 4. M. Latreche, PhD thesis, Universit Paul Sabatier, Toulouse, 1France, 1993 5. A. Sassela, A. Borghesi, F. Corni, A. Monelli, G. Ottaviani, 1R. Tonini, B. Pivac, M. Bacchetta, L. Zanotti, J. Vac. Sci. Technol. A 15 (2) 1(1997)

!!!! nemam clanek

6.1.4 Fainer03 /papers/hmdsn

XPS- It was revealed that all peaks consist of more than one Gaussian peak that indicate multi- ple bonding between the constituent atoms of Si,C and N.The Si 2p photo-electron peak could be resolved into two peaks centred at 100.3 -100.6 and 101.6 -101.8 eV,belonging to Si -C and Si -N bonding,respectively.The C 1s photoelectron peak consists of three components centred at 283.1-283.8, 284.5-284.8 and 285.7-286.1 eV, belonging to C-Si,C-C and C-N bonding [4,5].The N 1s photoelectron peak consists of one component centred at 397.3-397.6 eV,corresponding to N -Si bonding. Unfortunately,the present level of our understanding of the crystal structure of SiC x N y .lms is insuf .cient.We can propose that a plausible structure could be that of Si3 N4 in which some of the Si atoms are substituted by C atoms.

[4]M.T.Kim,J.Lee,Thin Solid Films 303 (1997)173. -bad refference, there is nothing about XPS [5]T.Tharigen,G.Lippold,G.V.Riede,et al.,Thin Solid Films 348 (1999)103.

6.1.5 Gengenbach99 /papers3/hmdsn

FTIR - XPS - detailed discussion! HMDSN: Some oxygen (O/Si 0.17) was detected in the freshly deposited film which might have been partially due to oxygen impurities in the discharge and/or to exposure to atmosphere. The O 1s BE of 532.3 eV, which was somewhat higher than expected for Si-O-Si probably indicated the presence of various oxygen-containing structures such as Si-O-Si, Si-O-C and O-C structures. A low concentration of C-O bonds was indicated by a weak C 1s signal detected at somewhat higher binding energy (about 1 to 2 eV) than the main carbon peak.

The chemical changes during storage for ppHMDSA were much more extensive compared to ppHMDSO. The O/Si ratio increased from 0.17 to about 1.15, accompanied by the almost complete loss of nitrogen, with N/Si decreas-ing from 0.36 to about 0.05, as shown in Fig. 5. A decrease of the C/Si ratio was also observed, from 2.24 to 1.75. The increase in O (DO/Si 0.98) was somewhat higher than the combined loss of N and C (DN/Si 1 DC/Si 20.80). In contrast to the corresponding ppHMDSO data, the O/Si ratio increased significantly during the first day (DO/Si 1 0.08 within the first five hours). This evolution is similar to the oxidative ageing of other plasma polymers, where the amount of oxygen incorporated (DO/C) during the initial, very rapid phase of oxidation was in the range 0.04 to 0.07 [18-20]. This first stage of oxidation after deposition was assigned to the quenching of radicals in the plasma poly-mers by O2 on exposure of the material to air. We therefore propose the same interpretation for the ppHMDSA coating.

More specific information was obtained by monitoring the evolution of peak shapes and BEs of the relevant photo-electron signals: Fig. 6 displays the BE values measured for the O 1s and Si 2p signals (referenced to C 1s at 284.40 eV). Whereas the O 1s BE did not change measurably, the Si 2p BE increased by approximately 1 eV to about 102.2 eV. The latter value is indicative of siloxane units. However, the overall Si 2p peak width increased from about 2.4 eV to approximately 2.7 eV during storage whereas in the case of the ppHMDSO coating this value remained unchanged at 2.3 eV. It follows that in the ppHMDSA material siloxane units were present in a variety of structural environments, in contrast to the ppHMDSO film which had a more uniform structure.

The N 1s signal developed into a doublet. The two components were quantified using the following curvefit protocol: all N 1s spectra were fitted with a two component model with the position of the two peaks being uncon-strained. Based on this first round of fitting, the mean peak separation determined was 2.28 eV $\pm$ 0.26 eV. All fits were then reoptimised with the separation of the two components fixed at that value. The BEs of the two components did not change during ageing within experimental uncertainty. While the original component at 398.0 eV (Si-N) lost inten-sity rapidly, a new component appeared at about 400.0 eV, increasing slowly in peak height until both peaks eventually displayed approximately the same, albeit weak, intensity (Fig. 5). The latter BE value is typical for aged alkyla-mine- based plasma polymers [19,20] and is characteristic of functional groups where the nitrogen is associated with oxygen on the same C atom, such as amide groups but is too low for oxidized N (nitrites, nitrates).

The C 1s peak, which initially had been symmetrical, developed a distinct tail at higher BE, evidence for some incorporation of oxygen into hydrocarbon structures. Since the additional C 1s components remained rather weak and were not clearly resolved, the newly formed carbon-oxygen-functional groups were quantified by C 1s curvefits using established values for the chemical shifts of C 1s BE compo-nents relative to aliphatic hydrocarbon at 285.0 eV (11.5 eV for C-O, 12.9 eV for C=O and 14.3 eV for O-C=O based groups) [28]. Thus, fits were calculated based on five components with fixed separations from the main peak (C-Si at 284.4 eV) of 10.6 eV (CHx), 12.1 eV (C-O), 13.5 eV (C=O) and 14.9 eV (O-C=O). For the C-O signal a value of 3.5% $\pm$ 1.0% of the total C 1s intensity was obtained. This value did not

change within experimental uncertainty over time. Fig. 7 displays the evolution of carbonyls/amides and acid/ester groups as a function of storage time. These data, which parallel oxida-tive changes in other plasma polymers [18,19] but are much less extensive, indicate that oxidation of hydrocarbon moieties occurred.

[1] Inagaki N, Kishi A. J Polym Sci, Polym Chem Ed 1983;21:2335. [2] Inagaki N, Kondo S, Hirata M, Urushibata H. J Appl Polym Sci 1985;30:3385. [18] Gengenbach TR, Vasic ZR, Chatelier RC, Griesser HJ. J Polym Sci, Part A: Polym Chem 1994;32:1399. [19] Gengenbach TR, Chatelier RC, Griesser HJ. Surf Interf Anal 1996;24:271. [20] Gengenbach TR, Chatelier RC, Griesser HJ. Surf Interf Anal 1996;24:611. [28] Beamson G, Briggs D. High resolution XPS of organic polymers. The Scienta ESCA300 database. 1st ed. Chichester, UK: John Wiley and Sons Ltd, 1992.

6.1.6 Grafting with HMDSN - citation?

2973 and 2914 cm^{-1} are ν(CH) stretching bands in $Si(CH_3)_3$, intense 1267 cm^{-1} is $\delta_s(CH_3)$, 3736 cm^{-1} is ν(OH) in Si-OH groups

6.1.7 Ungureanu03 (papers3/hmdsn)

3765 cm^{-1} OH stretching in isolated silanols (Si-OH), 3200-3600 cm^{-1} OH stretching in hydrogen-bonded silanols, 2975 cm^{-1} C-H stretching in methyl groups

6.1.8 Tanaka98

$Si-(CH_3)_3$ groups are hydrophobic.

6.1.9 Fainer03 (papers/hmdsn)

PECVD from HMDSN+NH_3, FTIR, XPS, elips, etc.

IR-spectra of silicon carbonitride films (HMDSN+He) synthe- sised in the temperature region of 473-773 K consist of the main adsorption band of 600–1200 cm^{-1},corresponding to the superposition of the Si-C (800 cm^{-1})and Si-N (900–950 cm^{-1}) stretching modes and the narrow peak at 1250 cm^{-1} presumably corresponding to the C-N stretching mode [Kim97,Tharigen99]. IR-spectra of the films grown at higher temperatures (773 -1173 K)consist of the wide band of 700 -1100 cm^{-1}.In addition, there is the narrow peak at 620 cm^{-1} ,correspond- ing to the disorder in SiC x N y .There are no hydrogenous bonds in the spectra.The band of 700 -1200 cm^{-1} was deconvoluted using Gaussian line shapes into the Si-C (800 cm^{-1})and Si-N (950 cm^{-1})bands. As seen from Fig.2a,the rise of the temperature up to 1123 K leads to a monotonic increase of the integral intensity ratio (I /I) in the IR-spectra.

XPS - The chemical compositions of the SiC x N y .lms determined by XPS are given in Table 2.It was shown that the concentration of oxygen is below 10 at%.The concentration of the main elements changes insignificantly with the synthesis tempera- ture rise.Binding energies of Si 2p,C 1s and N 1s core levels of this ternary compound are listed in Table 3.It was revealed that all peaks consist of more than one Gaussian peak that indicate multi- ple bonding between the constituent atoms of Si,C and N. The Si 2p photoelectron peak could be resolved into two peaks centred at 100.3-100.6 and 101.6-101.8 eV, belonging to Si-C and Si-N bonding, respectively. The C 1s photoelectron peak consists of three components centred at 283.1-283.8, 284.5-284.8 and 285.7-286.1 eV, belonging to C-Si,C-C and C-N bonding [4,5].The N 1s photo-electron peak consists of one component centred at 397.3-397.6 eV,corresponding to

References: [4] M.T.Kim,J.Lee,Thin Solid Films 303 (1997)173. [5] T.Tharigen,G.Lippold,G.V.Riede,et al.,Thin Solid Films 348 (1999)103.

Chapter 7

XPS - summary

7.1 CN_x films

[Dawei97] In either cubic or β phase C_3N_4, each C atom is sp^3 hybridized and σ-bonded with four N atoms, forming a tetrahedral configuration. As nitrogen has a greater electronic affinity, the electron cloud of the C-N covalent bond tends to move near the N atom. This transfer of negative charge increases the binding energy of the C(1s) and reduces the binding energy of the N(1s) electron (compared with that of the N_2 molecule).

In rhombohedral C_3N_4, each carbon atom is sp^2 hybridized and σ-bonded with three nitrogen atoms, making up a hexagonal structure. In the planar network of the hexagonal lattice, each atom, carbon or nitrogen, has a solitary electron, which form the π bonding between the interplanar C and N atoms (C=N bonds), making the structure a stable one similar to the benzene structure frequently found in organic compounds. Owing to the presene of C=N bonds, the rhombohedral C_3N_4 has the greatest chemical bond energy and therefore is chemically most stable among three C_3N_4 phases. [Dawei97]

About 30 papers dealing with CN films and XPS reffer to the urotropine. Some papers (Liu02,Lai03) reffer to Marton94 or accordingly with Marton94 to the comparision with urotropine and pyridine (Zheng96). Then the lowest BE assigned to C-N (sp^3), a little bit higher to C=N and the highest to N-N, N-O.

Other refferences are
Fernandez03 - Ref [29] J.C.Sanchez-Lopez,C.Donnet,F.Lefebvre,C.Fernandez- Ramos,A.Fernandez,J.Appl.Phys.90 (2001)675.

Sanchez-Lopez02 - Ref. [13] W.T. Zheng, H. Sjistrm, I. Ivanov, K.Z. Xing, E. Broitman, W.R. Salaneck, J.E. Greene and J.E. Sundgren. J Vac Sci Technol A 14 (1996), pp. 2696-2701.
Ref. [14] J. Wei, P. Hing and Z.Q. Mo. Wear 225/229 (1999), pp. 1141-1147.

Review of others in paper Bell01, Hammer01. Hammer01 is very good and detailed paper! They consider nitrile only for nitrogen rich samples. Cheng01 inform that C≡N in IF spectra at 2200 cm^{-1} is observed in N-rich samples.

HMDSO films (numbered): Alexander96 (well described including calibration), Alexander97a, Alexander97b (short), Aumaille00

HMDSN films: Fainer03, Gengenbach99 (detailed discussion), Tanaka98

7.2 Summary tables

My fit of APG films O1s:
one peak: 532.9 eV, FWHM 2.2 eV Anyway the BE is too high to be correct. We have to do some corrections and this support the assumption that main carbon peak belongs to C-Si and not to C-C bonds. In the FTIR we can see Si-OH bonds? Do we have also N-O bonds?

- 533.9 =¿ (cor. -0.3) 533.6 - SiO_2
- 532.9 (high) =¿ 531.7
- 531.5 =¿ 530.3

Table 7.1: XPS - C1s

ref.	BE [eV]	bonds
Song94 (in Bell01)	284	graphite
Song94 (in Bell01)	284.8	diamond
Gelius70	285.5	pyridine sp^2C-N
Barber73	286.9	urotropine sp^3 C-N
Lai03	284.5	free carbon peak
CN_x films	286.3	sp^2 C=N
	287.4	sp^3 C-N
Liu02	284.4	free carbon peak
CN_x films	285.6	sp^2 C=N
	287.3	sp^3 C-N
Fernandez03	284.6	pure graphitic sites in a-CN_x matrix + C-H contamination
CN_x films	285.9	CN bonding
	287.7	CN bonding
Sanchez-Lopez02	284.6	free pure carbon + adventitious C
CN_x films	285.9	sp^2 C=N ($\delta E = 1.3$ eV)
	287.7	sp^3 C-N ($\delta E = 3.1$ eV)
Bell01	284.4	pure carbon
CN_x films	285.1	sp^2 C=N ($\delta E = 0.7$ eV)
	287.8	sp^3 C-N ($\delta E = 3.4$ eV)
Marton94	284.6	adventitious carbon
CN_x films	285.9	sp^2 C=N ($\delta E = 1.3$ eV)
	287.7	β-C_3N_4 ($\delta E = 3.1$ eV)
	289.5	CO ($\delta E = 4.9$ eV)
Hammer01	284.3	graphitic C
CN_x films	285.2	aromatic C_3N
	286.2	non-aromatic C_3N includ. sp^3C-N (C_4N)
	287.4	non-aromatic C_2N_2
Chowdhury	286	sp^2 C=N
CN_x films *diff. approach*	288.5	sp C≡N
Riedo_applchem	284.4	graphite
pure DLC	285.2	diamond
Riedo_applchem	284.7	intermediate between sp^2 and sp^3
CN_x films	286.2	C=N ($\delta E = 1.5$ eV)
	287.3	C-N, C≡N ($\delta E = 2.5$ eV)
	288.7	C-O ($\delta E = 4$ eV)
Tharingen99	283.7	Si-C
SiCN hard films	284.5	C-C, amorphous free carbon
	285.5	C(sp^2)-N
	286.8	C(sp^3)-N
	288.6	C-O
Yu00	283.1	Si-C
SiC films	284.5	graphitic C
Kleps01	282.5	silicon carbide
SiC films	284.6	graphitic C
Zajickova01	284.8	C-C, C-H
	286.4	C-O ($\delta E = 1.6$ eV)
	288.6	C=O ($\delta E = 3.8$ eV)
	283.0	C-Si
Beamson, Briggs92	284.38	C in CH_3-Si environment
Alexander96	283.8	C in Si-CH_2-Si environment
	284.4	C in CH_3-Si or Si-$(CH_2)_2$-Si environment (in PDMS O-Si$(CH_3)_2$-O)
	284.7	C in phenyl carbon (radical from benzen)
	285	adventitious hydrocarbon contamination
Zuri96	284.4	C-Si
Gengenbach99	283.8	C-Si in Si-CH_2-Si
	284.4	C-Si in siloxanes
	285	CH_{rmx}, i.e.aliphatic hydrocarbons ($\Delta = 0.6$eV)
	286.5	C-O ($\Delta = 2.1$eV)
	287.9	C=O ($\Delta = 3.5$eV)
	289.3	O-C=O ($\Delta = 4.9$eV)
PP-HMDSO films	285	C-C
	286.5	C-O ($\delta E = 1.5$ eV)

Table 7.2: XPS - N1s

ref.	BE [eV]	bonds
Lindberg75 (in Marton94)	399.4	urotropine N-C sp^3
Boehland81 (in Marton94)	399.8 * pyridine N-C sp^2 aromatic!	
in Bell01	cca 398	C≡N (polyacrylonitrile)
Lai03	400.3	N-C sp^3
	401.7	N=C sp^2
Liu02	398.3	N-C sp^3
	400.2	N=C sp^2
Fernandez03	398.1	N-C sp^3 (urotropine)
	400.2	N=C sp^2 (pyridine)
Sanchez-Lopez02	399.1	N-C sp^3
	400.8	N=C sp^2
	402.7	N-O
Bell01	397.6	probably β-C_3N_4 written N-O, N-N
(no C≡N in IR+Raman)	399.1	probably C=N written C=N
!! errors in text	401.4	probably N-O, N-N, written β-C_3N_4
Marton94	398.3	β-C_3N_4
	400	N=C sp^2
	402	N-N, N-O
Hammer01-CN_x	398.3	N-sp^3C_3, sp^3N-C (non-aromatic) + (for N rich samples) N
	400.4	N-sp^2C
	402.4	N_2
Hammer01-azaadenine	398.6	CN¡
	399.3	pyridine (aromatic NC_2)
	400.1	N_2C (one double bond)
	400.7	-N_2C
	401.2	N_3 aliph. ($\approx NH_2$)
Hammer01-CN_x:H	398.7	non-aromatic NC_2, NC_3
	399.3	pyridine (aromatic NC_2)
	400.3	N_2C aliph.
	401.2	N_3 aliph. ($\approx NH_2$)
	402.4	N_2 molecule
other approach		
Chowdhury99	398.8	C≡N
	400	N-C sp^2
Beamson, Briggs92	398.9	sp^3 C-N
	400.2	C=N
	397.48	Si_3N
Gengenbach99	397.8	N-Si, recherche
	398	Si-NH-Si, fresh
	400.0	aged alkyl-amine polymers, functional group N-
	¡ 400	oxidized N (nitrites, nitrates)

Table 7.3: XPS - Si2p

ref.	BE [eV]	bonds
Zajickova01	103	SiO_4
	101.4-100.7	SiO_xC_y
	99.9-99.6	Si-Si
Fourches93	103.5	SiO_4
	102.3	SiO_x
	101.3	SiO_xC_y
	100.3	SiC
Gao00 (SiCN films)	101.7	Si-N, Si-O
Gong99 (SiCN films)	101.5	Si-N
	99.2	Si-C, Si-Si
Alexander96	103.4	silica SiO_4
	102.1	PDMS O-Si$(CH_3)_2$-O
	101.8	PP-HMDSO Si$(CH_x)_yH_z$-O ($y+z=3$)
Gengenbach99	100.6±0.38	≡Si-Si≡, ≡Si-C≡
	101.2 N/A	=N-Si≡ recherche
	101.2	Si-NH-Si
	102.15±0.36	[-Si$(CH_3)_2$-O-]$_n$ (siloxane)
	103.49±0.13	SiO_2 (silica), -O-Si(O)-O-
Beamson & Briggs	102.40	Si $2p_{1/2}$ in PDMS
	101.79	Si $2p_{3/2}$ in PDMS, main peak
	102.29	Si $2p_{1/2}$ in PPMS
	101.68	Si $2p_{3/2}$ in PPMS, main peak

Table 7.4: XPS - O1s

ref.	BE [eV]	bonds
Alexander96	532.4	Si-O-Si in PPMS, PPDMS
	532.6	Si-O-Si in quartz
Perkin-Elmer	532.5-533.2	SiO_2
	532.5-533.7	nitrates
	530.9-532	hydroxides
	530.5-531.5	carbonates
Aumaille00	532.7	O_4Si
Gengenbach99(rech)	532.93±0.34	SiO_2 (silica)
	532.11±0.12	[-Si$(CH_3)_2$-O-]$_n$ (siloxane)
Beamson & Briggs	532.00	Si-O-Si in PDMS or PPMS
	532.64	C-O-C aliphatic in CHO polymers, e. g.C-C-O-C-C
	532.89	C-OH aliphatic in CHO polymers
	533.15	O-C-O in CHO polymers, e. g.C-C-O-C-O-C
	531.1	C-O-C in PEOx,i. e.C-C-O-C-N_2C
	531.3–531.9	O=C-N, e. g.polyacrylamide O=C(CN)

7.3 My fit of XPS on HMDSO and HMDSN APG films

N1s:

- 401.2 - sp^3 N bonded to some hydrogen → korekce 400.8
- 400.1 - N-sp^2C → korekce 399.7
- 398.6 - N-sp^3C → korekce 398.2

other possibility FWHM=1.6 fixed

- 401.5 → 401.2 - sp^3 N bonded to some hydrogen
- 400.1 → 399.8 - N-sp^2C
- 398.8 → 398.5 - N-sp^3C

C1s: (varianta c2) FWHM=1.6eV fixed

- 284.4 - CH_3-Si; real position 284.7 → correction -0.3
- 285 - C-C, C-H ($\delta E = 0.6$ eV); fixed real position 284.7+0.6=285.3
- 286.4 - C-O (286.5-286.6, $\delta E' = 1.5$–1.6 eV)), C=N (286.3, $\delta E' = 0.7$, 2x**1.3**, 1.5 eV); free real pos. 286.7 ($\delta E = 2.0$ eV)
- 287.7 - sp^3C-N ($\delta E' = 2.5$, 3.1, 3.4 eV); free real pos. 288 ($\delta E = 3.3$ eV)
- 288.8 - C=O ($\delta E' = 2.9$, 3.8, 4, 4.9 eV); free real pos. 289.1 ($\delta E = 4.4$ eV)

(varianta) FWHM=1.6eV fixed

- 284.4 - CH_3-Si; real position 287 → correction -2.62
- 285.8 - C-O (286.5-286.6, $\delta E' = 1.5$–1.6 eV)), C=N (286.3, $\delta E' = 0.7$, 2x**1.3**, 1.5 eV); contribution of C-C, C-H free real pos. 288.4 ($\delta E = 1.5$ eV)
- 287.4 - sp^3C-N ($\delta E' = 2.5$, 3.1, 3.4 eV); free real pos. 288 ($\delta E = 3.1$ eV)
- 288.9 - C=O ($\delta E' = 2.9$, 3.8, 4, 4.9 eV); free real pos. 289.1 ($\delta E = 4.4$ eV)

(varianta c3) FWHM=1.7eV fixed

- 284.4 - CH_3-Si; real position 284.9 =¿ poloha 283.2
- 285 - C-C, C-H ($\delta E = 0.6$ eV); real position 286.2 (1.3) =¿ nabijeni -1.2
- 286.4 - C-O (286.5-286.6, $\delta E' = 1.5$–1.6 eV)), C=N (286.3, $\delta E' = 0.7$, 2x**1.3**, 1.5 eV); real pos. 287.6 (1.4) =¿ poloha 286.4
- 288.1 - sp^3C-N ($\delta E' = 2.5$, 3.1, 3.4 eV); real pos. 288.9 (2.7) =¿ poloha 287.7
- not taken into account 288.8 - C=O ($\delta E' = 2.9$, 3.8, 4, 4.9 eV); real pos. 290.1, outside the range! =¿ 288.9
- 289.3 - O-C=O

Si2p: The highest BE is for silica (SiO_4) at 103.5 eV.

- 103.5 - silica (SiO_4)
- 102.5 - SiO_x
- 101.1 - Si-N

Table 7.5: Fits of XPS N1s signal

sample	peak	area	position [eV]	FWHM [eV]	%Lorentz
HMDSO1	0	401.186	1436.585	1.900	0
	1	399.944	5246.289	1.700	0
$\chi = 12.0$	2	398.642	2393.655	1.500	0
HMDSO4	0	401.068	2761.824	1.900	0
	1	399.867	7468.423	1.700	0
$\chi = 45.6$	2	398.541	3184.302	1.565	0
HMDSN1	0	400.847	4650.752	1.700	0
	1	399.909	12463.39	1.700	0
$\chi = 45.6$	2	398.787	9291.873	1.700	0
HMDSN2	0	401.134	1187.135	1.700	0
	1	399.935	4297.403	1.700	0
$\chi = 16.7$	2	398.706	2615.157	1.700	0
HMDSN3	0	401.089	3267.035	1.700	0
	1	400.235	8687.732	1.700	0
$\chi = 40.5$	2	399.159	9779.181	1.700	0
HMDSN4	0	400.700	3200.000	1.700	0
byt fixni, proc?!	1	399.500	6483.166	1.700	0
$\chi = 88.9$	2	398.198	1579.909	1.700	0
HMDSN5	0	401.312	1628.066	1.700	0
	1	399.987	7062.621	1.700	0
$\chi = 16.4$	2	398.677	3645.203	1.700	0

Chapter 8

Infrared absorption - summary

[?]: All the FTIR spectra exhibit a sloping baseline due to an optical interefence effect, which has been removed by fitting the experimental curve in the transparent region. The normalized absorbance spectra were obtained by converting the corrected transmission spectra to absorbance spectra and dividing the result by film thickness (determined using spectroscopic ellipsometry).

8.1 Good papers specific to FTIR

Papers with FTIR on HMDSN films:

- Seekamp00 (paper3/hmdsn) - see text above
- Liang03 (papers3/hmdsn)
- gonzalez_luna98 (papers3/hmdsn)
  Deposition of silicon oxinitride films from hexamethyldisilizane (HMDS) by PECVD, Thin Solid Films, Volume 317, Issues 1-2, 1 April 1998, Pages 347-350 R. Gonzlez-Luna, M. T. Rodrigo, C. Jimnez and J. M. Martnez-Duart

Papers with FTIR on CSi_xN_y films:

- Tharigen99 (papers/sicn) - CSixNy films, XPS, FTIR etc. Table 3. FTIR absorption lines (cm-1) of CSixNy films deposited from graphite targets with 0

Papers with FTIR on CN_x films:

- Jelinek00 (papers1/cn)
- Mutsukura

8.2 Summary tables

assigment	absorption band [cm^{-1}]
C-H asym. str.	2960-2950
C-H sym. str.	2910-2890
Si-H str. in SiH_x	
$-CH_3$ sym. def. in $Si(CH_3)_x$	1010-980
$-CH_2-$ wagging in $Si-CH_2-Si$	
Si-O-Si and/or Si-O-C str.	
Si-C str	830-800
Si-Si asym str	455

Table 8.1: Infrared Absorption Bands in spectra of TMSS - Wrobel

Table 8.2: Infrared Absorption Bands of methylsilyl group - Organometalic Che. Rev. 68., Horak

compound	vibration	wavenumber	ref.
-CH_3	$\nu_{as}(CH_3)$	2950-2973	Organometal. Chem. Rev. 196
-CH_3	$\nu_{s}(CH_3)$	2895-2913	Organometal. Chem. Rev. 196
-CH_3	$\delta_{as}(CH_3)$	1395-1465	Organometal. Chem. Rev. 196
-CH_3	$\delta_{s}(CH_3)$	1240-1285	Organometal. Chem. Rev. 196
-CH_3	$\rho_{as}(CH_3)$	800-900	Organometal. Chem. Rev. 196
-CH_3	$\rho_{as}(CH_3)$	750	Organometal. Chem. Rev. 196
-$SiCH_3$ char. for -$Si(CH_3)_x$	$\delta_{s}(CH_3)$	-$\approx$ 1250	
-$Si(CH_3)_3$	$\delta_{s}(CH_3)$	1250	HMDSO1
HMDSO	$\delta_{s}(CH_3)$	1252	Organometal. Chem. Rev. 196
area $\approx$ 800 decides among RSi, R_2Si and R_3Si			
-$Si(CH_3)_3$	$\rho_{as}(CH_3)$	$\approx$ 850	Organometal. Chem. Rev. 196
HMDSO	$\rho_{as}(CH_3)$	843	Organometal. Chem. Rev. 196
-$Si(CH_3)_3$	$\rho_{s}(CH_3)$	$\approx$ 750	Organometal. Chem. Rev. 196
HMDSO	$\rho_{s}(CH_3)$	756	Organometal. Chem. Rev. 1968, HM
-$Si(CH_3)_3$	$\nu_{as}(SiC_3)$	$\approx$ 700	Organometal. Chem. Rev. 196
-$Si(CH_3)_3$	$\nu_{s}(SiC_3)$	600-660	Organometal. Chem. Rev. 196
-$Si(CH_3)_2$	$\rho_{s,as}(CH_3)$	800-850	Organometal. Chem. Rev. 196
-$Si(CH_3)_2$	$\rho(CH_3)$	800	HMDSO16
-$Si(CH_3)_2$	$\nu_{as}(SiC_2)$	760-820	Organometal. Chem. Rev. 196
-$Si(CH_3)_2$	$\nu_{s}(SiC_2)$	650-700	Organometal. Chem. Rev. 196
-$Si(CH_3)$	$\rho(CH_3)$	$\approx$ 800	Organometal. Chem. Rev. 196
-$Si(CH_3)$	$\nu(SiC)$	$\approx$ 750	Organometal. Chem. Rev. 196
CH_3SiH_3	sym. deformation CH_3	1266	
CH_3SiH_3	rocking CH_3	870	
CH_3SiH_3	stretching Si-C	701	

Table 8.3: Infrared Absorption Bands in n-alkane - Horak

compound	vibration	wavenumber
CH_3	asym. stretching	2958-2954
CH_2	asym. stretching	2927
CH_3	sym. stretching	2872-2869
CH_2	sym. stretching	2855-2853

Table 8.4: Infrared Absorption Bands in liquid HMDSO and HMDSN -Organometalic Che. Rev. 68.

wavenumber	monomer	vibration
3385	HMDSN	N-H
2962	HMDSN	$\nu_{as}(CH_3)$
2956	HMDSO	$\nu_{as}(CH_3)$
2903	HMDSN	$\nu_s(CH_3)$
2899	HMDSO	$\nu_s(CH_3)$
1402	HMDSN,HMDSO	$\delta_{as}(CH_3)$
1437	HMDSN,HMDSO	$\delta_{as}(CH_3)$
1252	HMDSO,HMDSN	$\delta_s(CH_3)$
843(main)	HMDSO,HMDSN	$\rho_{as}(CH_3)$
752	HMDSO	$\rho_s(CH_3)$
759	HMDSN	$\rho_s(CH_3)$
690	HMDSN	$\nu_{as}(SiC_3)$
683	HMDSO	$\nu_{as}(SiC_3)$
618	HMDSO, HMDSN	$\nu_s(SiC_3)$
565	HMDSN	$\nu_s(Si_2N)$
932	HMDSN	$\nu_{as}(Si_2N)$

Table 8.5: Infrared Absorption Bands in amines - Horak str. 212-216

compound	vibration	wavenumber	comment
methylamin CH_3NH_2 (gas)	asym. stretching NH_2	3427	
methylamin CH_3NH_2 (gas)	sym. stretching NH_2	3361	
methylamin CH_3NH_2 (gas)	def. NH_2	1623	
methylamin CH_3NH_2 (gas)	twisting NH_2	1015 cal.	
methylamin CH_3NH_2 (gas)	stretching C-N	1044	
methylamin CH_3NH_2 (gas)	wagging NH_2	780	
methylamin CH_3NH_2 (gas)	torsion	270	
methylamin CH_3NH_2 (gas)	asym. stretching CH_3	2985	
methylamin CH_3NH_2 (gas)	sym. stretching CH_3	2961	
methylamin CH_3NH_2 (gas)	sym. stretching CH_3	2820	
methylamin CH_3NH_2 (gas)	asym. deformation CH_3	1485 cal.	
methylamin CH_3NH_2 (gas)	sym. deformation CH_3	1473	
methylamin CH_3NH_2 (gas)	sym. deformation CH_3	1430	
methylamin CH_3NH_2 (gas)	rocking CH_3	1195 cal.	
methylamin CH_3NH_2 (gas)	rocking CH_3	1130	
RNH_2 (liquid)	asym. stretching NH_2	3392-3382	
RNH_2 (liquid)	sym. stretching NH_2	3327-3317	weaker than asym.
RNH_2 (liquid)	deformation NH_2	$\approx$ 1620	in monoamines and α,ω-diamines
RNH_2 (liquid)	deformation NH_2	840-810, 793-763	in amines RCH_2NH_2 (R is alkyl)
RNH_2 (liquid)	deformation NH_2	851-829, 810-778	in amines R_2CHNH_2
RNH_2 (liquid)	deformation NH_2	851-815, 784-768	in amines R_3CNH_2
RNH_2 (liquid)	torsion NH_2	¡290	
RNH_2 (liquid)	stretching CN	1090-1068	in amines RCH_2NH_2
RNH_2 (liquid)	stretching CN	1043-1037	in amines R_2CHNH_2
RNH_2 (liquid)	stretching CN	1038-1022	in amines R_3CNH_2
dimethylamin (liquid)	stretching NH	3294	
dimethylamin (liquid)	deformation NH	724	

Table 8.6: Infrared Absorption Bands in SiN, SiC and SiCN materials.

compound	vibration	wavenumber	ref.
a-Si_3N_4	Si-N	450	Liang03-11
a-Si_3N_4	Si-N	950 broad	Liang03-11
a-Si_3N_4	$CH_{3,2,1}$	1250, 1300	Liang03
a-Si_3N_4	$NH_{3,2,1}$	3400	Liang03
a-Si_3N_{4-x}	Si-N stretching	880	Lattemann03-7
a-Si_3N_{4-x}	Si-N breathing	490	Lattemann03-17
a-Si_3N_{4-x}	Si-N_2 stretching (trapped N)	2335-2360	Lattemann03-18
SiC	Si-C stretching	782-794, double peak 800+890	Lattemann03-19,20

assigment	absorption band [cm^{-1}]	ref.	liquid HMDSO	HMDSO film	O_2/HMDSO high
O-H stretch.	3650	HMDSO16	no	no	no
in isolated SiOH groups		HMDSO19-24	-	weak	yes
O-H stretch in SiOH species	3450	HMDSO19-24	-	weak	yes
OH	3400–3200, 3200–2500(?)	HMDSO1	yes	no	yes
Si-OH	3250	HMDSO1	no	yes	no
C-H asym. str.	2960	HMDSO16,19	yes	yes	no
C-H str. in CH_3	2960	HMDS09	-	yes	-
C-H str.	2930	HMDSO19	-	yes	no
C-H sym. str.	2880	HMDSO16	yes	yes	no
C-H sym. str.	2900	HMDSO19	-	yes	no
C-H str. in CH_2	2900	HMDSO9	-	yes	-
CH_3	2975–2945, 2885–2855	HMDSO1	yes	no	no
Si-H	2250 $\rightarrow$ 2150	HMDSO19	-	yes	from 33%
Si-H	2300–2100	HMDSO1	yes($\downarrow$)	yes ($\uparrow$)	no
Si-H in Si-H_x	2100	HMDSO9	-	yes	-
Si-$(CH_2)_x$-Si	1400	HMDSO19-15	-	yes	no
Si-$(CH_2)_x$-Si	1360	HMDSO19-15	-	yes	no
Si-CH_3 bending	1270	HMDSO16,16-28,16-29	yes	yes	no
Si-CH_3 sym. def.	1260-1250	HMDSO14,14-18	-	yes	-
Si-$(CH_3)_x$	1250	HMDSO1,19-15	-	yes	no
Si-CH_3	1250	HMDSO9	-	yes	-
Si-O-Si stretch.	1070	HMDSO16	yes	yes	yes
Si-O-Si	1090–1020	HMDSO1,9	yes	yes	yes
Si-O-C	1090-1020	HMDSO1,9,14,14-17			
SiO-CH_3	1000-1100	HMDSO9	-	yes	-
Si-CH_2-Si wagging	1090-1020	HMDSO14,14-14,14-15	-	yes	-
Si-CH_3 rocking	990-980	HMDSO14,14-16	-	yes -	
Si-OH bending	930	HMDSO16	no	no	no
Si-$(CH_3)_x$	890	HMDSO19-15	-	yes	no
Si-$(CH_3)_3$ rocking	840	HMDSO16,16-28,16-29	yes	yes	
Si-$(CH_3)_x$	810	HMDSO19-15	-	yes	no
Si-$(CH_3)_2$	814–800	HMDSO1	yes	yes	yes
Si-CH_3 stretch.	800	HMDSO1,16,16-28,16-29	yes	yes	
Si-$(CH_3)_2$ rocking	800	HMDSO16,16-28,16-29	yes	yes	
Si-O-Si bending	800	HMDSO16	?	?	yes
Si-CH_2	800	HMDSO9	-	yes	-
Si-$(CH_3)_3$	755	HMDSO1	yes	no	no
Si-O-Si rocking	450	HMDSO16	?	?	yes
Si-O-C	500-300	HMDSO1	yes	yes	yes

Table 8.7: Infrared Absorption Bands in spectra of HMDSO. Data for Si-$(CH_3)_x$ are taken from [5], [6]. Si-OH groups are generally responsible for siloxane film aging. x =1,2,3

assigment	absorption band [cm^{-1}]	ref.	where
Si-CH_3 deformation	1260	Seekamp00_6	HMDSN+HMDS films
Si-CH_2-Si	1240	Seekamp00_6	HMDSN+HMDS films
Si-$(CH_3)_3$ rocking	840	Seekamp00_6	HMDSN+HMDS films
Si-$(CH_3)_2$ stretching	790	Seekamp00_6	HMDSN+HMDS films
Si-CH_3 stretching	775	Seekamp00_6	HMDS films
Si-$(CH_3)_4$	695	Seekamp00_6	TMS
Si-N-Si asym. stretching	923	Seekamp00_6	HMDSN liquid+films, heptaMDSN
Si-NH-Si bending	1184	Seekamp00_6	HMDSN liquid+films, heptaMDSN
Si-N	950 broad	Liang03_11	a-Si_3N_4
Si-N	450	Liang03_11	a-Si_3N_4
$\nu_s(Si_3N)$	438	Organomet. Chem. Rev. 1968	$(R_3Si)_3N$
$\nu_{as}(Si_3N)$	916	Organomet. Chem. Rev. 1968	$(R_3Si)_3N$
CH_x	1250	Liang03	Si_3N_4 powder
CH_x	1300	Liang03	Si_3N_4 powder
S-C	800 broad	Liang03	SiC powder
N-H_x, O-H	3400	Liang03	Si_3N_4 powder
Si-OH	3738	Baraton03	
C=C, C=N, N-H, O-H	1600-1630	Jelinek00	CN_x films
N-H, O-H	3300	Jelinek00	CN_x films
-C≡N nitrile	2220-2230 cm-1	Jelinek00	CN_x films
-N≡C isonitrile	2115-2175 cm-1	Jelinek00	CN_x films
-N=C=N- carbodiimide	2105-2155 cm-1	Jelinek00	CN_x films
N-H stretching	3200, 3300, 3450	Mutsukura99	¿NH, -NH_2 in CN_x films
C=C, C=N stretching, N-H bending	1500-1800	Mutsukura99	CN_x films
C-H stretchign	2800-3000	Mutsukura99	CN_x films
C-H, C-N	1300-1500	Mutsukura99	CN_x films
C=C	1680	Mutsukura99	CN_x films
-C≡N in alyphatic	2245-2255	Mutsukura99	CN_x films
-C≡N in aromatic	2226-2229	Mutsukura99	CN_x films
-N≡C in alyphatic	2146-2183	Mutsukura99	CN_x films
-N≡C in aromatic	2122-2125	Mutsukura99	CN_x films

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