



Structural characterization of amorphous hydrogenated-carbon nitride (aH-CN_x) film deposited by CH₄/N₂ dielectric barrier discharge plasma: ¹³C, ¹H solid state NMR, FTIR and elemental analysis

Abhijit Majumdar^{a,*}, Gudrun Scholz^b, Rainer Hippler^a

^a Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany

^b Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor Str. 2, 12489 Berlin, Germany

ARTICLE INFO

Article history:

Received 20 May 2008

Accepted in revised form 24 January 2009

Available online 6 February 2009

PACS:

52.25.Mq

82.80.Gk

73.50.Td

68.55.Nq

82.80.-d

36.20.Hb

68.35.Dv

Keywords:

Dielectric barrier discharge (DBD)

Hydrogenated carbon nitride film (aH-CN_x)

NMR

FTIR spectroscopy

Elemental analysis (chemical)

ABSTRACT

The chemical composition and bond structure of polymer like amorphous hydrogenated carbon nitride (aH-CN_x) thin films was studied by solid-state ¹³C and ¹H MAS NMR spectroscopy, FTIR spectroscopy and elemental analysis. The hydrogenated CN_x film was deposited on Si (100) substrate by CH₄/N₂ gas mixture dielectric barrier discharge (DBD) plasma. The broad ¹H signals obtained even at 33 kHz spinning speed with spinning side bands indicates the existence of a large proton proportion in the film. The ¹H and ¹³C signals are strongly broadened due to homo- and heteronuclear dipolar couplings and also due to amorphous nature of the deposited film. The local structure of the amorphous aH-CN_x film is dominated by C–C and C–N single bonds i.e. carbon is mainly in the sp³ hybridized state. The Fourier Transform infrared (FTIR) spectroscopy of the film indicates the typical regions for –C≡N, –(C=O), –NH, vibrations together with overlapping NH and OH stretching bonds. CH₃ and C–N groups as well as species with C=N conjugated double bonds are present in the deposited CN_x film. From elemental analysis it is obtained that the composition of the film is (in wt.%): C: 61.8, H: 8.4, N: 17.7.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Amorphous hydrogenated-carbon nitride (aH-CN_x) films have been attracting great interest for industrial applications mainly because of their excellent mechanical, tribological and optical properties as well as in biomedical application. In addition, they are chemically inert. The hardness and elastic property of the a-CN_x film have been studied widely. So far it is mostly proposed that CN_x films consist of graphite-like bonds (carbon in sp² hybridization) with incorporated nitrogen which is crosslinked with sp³ hybridized C sites [1]. The relative fractions of sp² and sp³ hybridized carbon in amorphous CN_x have been studied by electron energy loss spectroscopy (EELS) [2–4] and near-edge X-ray absorption fine-structure spectroscopy (NEXAFS) [5]. However till to date, no concrete quantitative measurements of the amount of sp²/sp³ hybridized carbon and possible structural chemical formula have been reported in the literature.

Carbon nitride films have been fabricated by various techniques such as: plasma enhanced chemical vapor deposition (PECVD) [6,7], chemical vapor deposition (CVD) [8], magnetron sputtering [1], ion beam assisted deposition [9,10], pulsed laser deposition [11,12], or dielectric barrier discharge (DBD) plasma [13,19,20,33]. Mostly previous research work is focused towards the combination of sp, sp², and sp³ hybridized structure in hydrogenated CN_x films and relatively hard and elastic materials as it is theoretically estimated that the beta-carbon nitride film is harder than diamond [14]. Still to date several works have been published on the basis of hardness, elasticity, graphite (sp²) band orientation and also nanocrystalline diamond structure of the CN_x film [1,5,15]. In our previous work the layer thickness, refractive index, quantitative description of the film surface and chemical composition of the amorphous H-CN_x film have been mentioned [13]. It was found in AFM, that the deposited hydrogenated carbon nitride film is amorphous and inhomogeneous in nature. However, most of the earlier NMR work on carbon nitride film has been focused on hard/elastic hydrogenated materials, hydrogenated carbon materials deposited at ambient temperature. The focus of this report is more on a hydrogenated amorphous carbon nitride film which is a polymer like soft film rather than hard film [8,13,16–18]. At

* Corresponding author. Tel.: +49 3834864784; fax: +49 3834864701.

E-mail address: majumdar@physik.uni-greifswald.de (A. Majumdar).

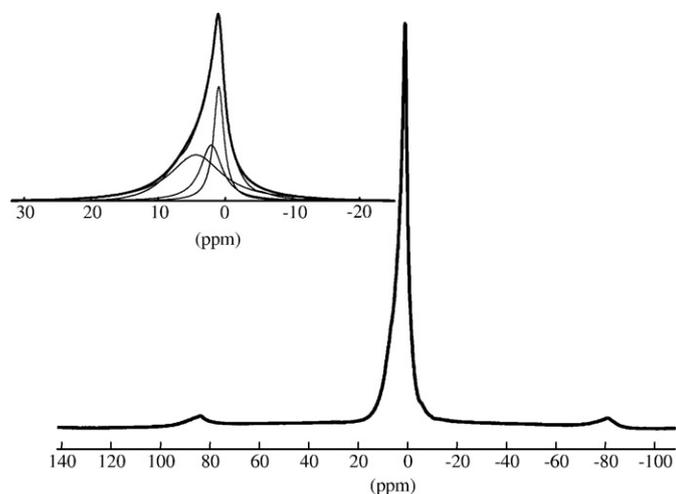


Fig. 1. ^1H MAS NMR spectrum of aH-CN $_x$ taken at 33 kHz spinning speed. (Spinning side bands are indicated with asterisks; the central line is given with its decomposition as insert).

present, the results of the solid state ^1H and ^{13}C MAS NMR of an amorphous hydrogenated CN $_x$ film deposited by DBD plasma, interestingly differ from those of others previous research works.

In this paper, we report the solid state ^{13}C , ^1H MAS NMR, FTIR and elemental analysis results on an aH-CN $_x$ film deposited by CH $_4$ /N $_2$ DBD plasma which is a polymer like film and exhibits broadened overlapped spectra of several bands.

The solid-state nuclear magnetic resonance (NMR) spectroscopy is used to distinguish between different ^1H and ^{13}C sites if possible compared to results of FTIR spectroscopy. Elemental analysis allows the quantitative determination of carbon, nitrogen and hydrogen present in the aH-CN $_x$ film.

2. Experimental

The aH-CN $_x$ film was deposited on 20 mm diameter p-type Si (100) substrate as well as the dielectric electrodes (upper electrode is Al $_2$ O $_3$ and ground electrode is glass) by CH $_4$ /N $_2$ DBD plasma. The Si wafer was used as dummy substrate and it is located on the glass electrode. The experiment was performed at a pressure of 300 mbar and with a CH $_4$ /N $_2$ mixture ratio at 1:3. The experimental set up has been explained in details elsewhere [19,20]. The electrical power consumed during experiment was 5 W, where the peak to peak voltage was 10.5 kV at 5.5 kHz.

For the NMR analysis, 9 μm -thick film was obtained by 8 h deposition. The 200 mg material was subsequently scraped off from the electrode substrate. The same material was used for the elemental analysis. The film deposited on Si (100) wafer was used for FTIR spectroscopic measurement. The deposited film was investigated by means of the following techniques.

^1H and ^1H - ^{13}C CP MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Larmor frequencies: $\nu_{^1\text{H}}=400.2$ MHz, $\nu_{^{13}\text{C}}=100.6$ MHz) using both a 2.5 mm and a 4 mm MAS probe (Bruker Biospin). The applied spinning speeds are given in the caption to the figures. ^1H MAS studies were made with a $\pi/2$ pulse length of 3.2 μs and a recycle delay of 10 s (16 accumulations). Existent background signals of ^1H could be completely suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [21]. The contact times of the ^1H - ^{13}C CP MAS NMR experiments were optimized as 500 μs , the recycle delay was 10 s and the experiment was performed with an accumulation number of 7100. Values of the isotropic chemical shifts of ^1H , and ^{13}C are given with respect to TMS.

Fourier transform infrared (FTIR) transmission spectra were obtained by means of FTIR spectrometer Bruker (Vector 22). The

plain sample was placed in a vacuum chamber built into the spectrometer in order to minimize the IR signal of water vapor, CO $_2$ content and noise. The measuring signal passed the optical way with an aperture diameter of 3 mm with spectral resolution 4 cm $^{-1}$. For optimal signal-to-noise ratio 50 scans were averaged per sample spectrum and apodized by applying of the Norton Beer apodization function for Fourier transformation. Interferograms were zero-filled using a zero-filling factor of 2. The background spectrum was measured on a pure silicon substrate independently.

The elemental analysis of the samples was performed with a LECO CHNS-932 combustion equipment (C, H, N).

3. Results and discussions

3.1. ^{13}N and ^1H nuclear magnetic resonance

Fig. 1 shows the ^1H MAS NMR spectrum of the deposited carbon nitride film recorded at a spinning speed of 33 kHz. The central line of the spectrum given in Fig. 1 is broad and together with the still visible spinning side bands it indicates the existence of a large number of protons in the deposited film. The spectrum can be simulated taking into account three different lines with Lorentzian line shape at 0.9 ppm (24.5%), 2.0 ppm (25.2%) and 4.3 ppm (50.3%). The narrow line at 0.9 ppm is in the typical area of -CH $_3$ groups, but also non-bridged -OH groups at the surface may contribute to this signal [21,22]. The more low-field shifted signals cover the range of -O-CH $_2$ -, CH-O, CH $_2$ -N, or C-NH $_2$ units in the matrix. However, also surface adsorbed water molecules can give a pronounced contribution to the broad signal at about 4 ppm in addition [21,22]. The latter was shown for another (CN) $_x$ sample by Gammon et al. [23].

Fig. 2 shows the ^1H - ^{13}C CP MAS NMR spectrum taken in the 4 mm probe with a spinning speed of 10 kHz. Two main signal areas can be assigned, one at 173 ppm and a broad, slightly structured signal between 10 ppm and 60 ppm, with an asymmetric tail in the low-field part of this signal. The spinning side bands are indicated in addition. Due to the amorphous, disordered nature of this sample, the observed signals are broad, overlapped and only hardly to assign. The main intensity of the spectrum lies in the range between 10 and 80 ppm. In contrast to and in comparison with previously published studies on amorphous (CN) $_x$ films [1] it is obvious that the present aH-(CN) $_x$ sample is dominated by CH $_3$ -C or CH $_3$ -N units giving resonances between about 10 and 40 ppm. This means, carbon is mainly in the sp 3 hybridized state. The signal area between 40 and 80 ppm may be due to contributions of C-N single bonds with lower proton content at the carbon atoms. Moreover, comparing the chemical shift region around 150 ppm (Fig. 2) with previous results [1], C=N double bonds are less probable in the sample. However, an additional signal at \sim 173 ppm

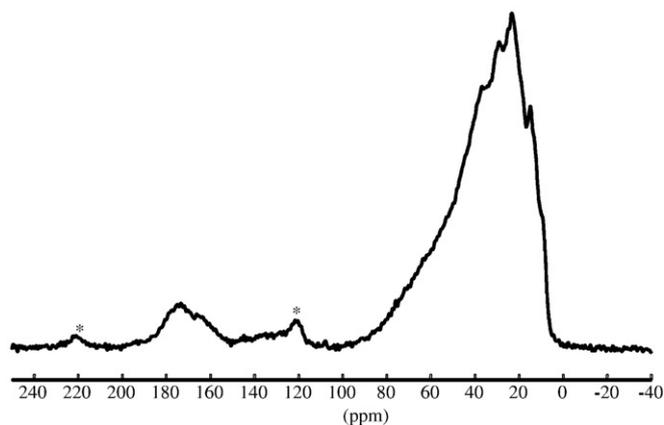


Fig. 2. ^1H - ^{13}C CP MAS spectrum of the aH-CN $_x$ film taken at 10 kHz. The resolved spinning side bands are indicated as asterisks.

supports the existence of few C=O groups. Due to an overlap with spinning side bands in the region at 120 ppm, a possible existence of few C≡N triple bonds may be covered.

3.2. Fourier transforms infrared spectroscopy (FTIR)

The nature of the deposited films required a spectral allowance for an extinction inhomogeneity across the surface and long wave interference effects in the bulk. Therefore base line correction of the recorded spectra was performed by the concave elastic band method. Typical IR transmission spectra are shown in Fig. 3, within the range from 4000 cm⁻¹ to 700 cm⁻¹. According with the Bouguer–Lambert–Beer law the interval of integral absorption coefficient $(2.6 \pm 1.5) \times 10^4$ m⁻¹ is characteristic for all deposited layers. The transmission spectrum of the deposited hydrogenated carbon–nitride films is characterized by several typical spectral regions. The band between 3100 cm⁻¹ and 3700 cm⁻¹ is attributed to stretching vibrations of NH and OH functionally groups [13,24,25].

The region 3140–3500 cm⁻¹ is attributed as overlapping NH and OH band. More precisely, in the region 3300–3490 cm⁻¹ is referred as anti-symmetric NH₂ stretching band and at 3140 to 3300 cm⁻¹ is H bonded NH symmetric stretching band. However the separation of the overlapped bands is very complicated due to intermolecular interactions as H-bridges, which are very intensive in this region and cause the broadening of the bands. There are two consecutive intervals that appeared at 2965 cm⁻¹ and 2884 cm⁻¹ which are attributed to –C-CH₃ and ≡CH band respectively [26]. The intensity of the bands is low (absorption up to 1%) and is related with the concentration of methane in the gas discharge. In addition to this, we note (see Fig. 3) a fine absorption band around 1600 cm⁻¹ that is due to the sp² carbon and is normally IR forbidden [25]. The appearance of this feature suggests that the incorporation of nitrogen breaks the sp² symmetry and makes this feature IR active [27,28]. The band from 2250 cm⁻¹ to 2100 cm⁻¹ is triple bond configuration and absorption peak at 2185 cm⁻¹ is conjugated stretching vibration band so called nitrile group (–C≡N). The region from 1580 cm⁻¹ to 800 cm⁻¹ is characterized by a large number of banding vibrations and intermolecular interactions. Absorption in this region can be interpreted as quality of cross-linking of the deposited structure. However, any qualitative properties of the region are pointed. The board band including the region at 1600 to 1635 cm⁻¹ usually referred as the band of water molecule deformation vibrations and generally it is weak band [29]. But the appearance of deformation H₂O band is pressure dependent and it appear at GPa, high pressure range (low vacuum) where our experimental condition is at low pressure (~300 mbar or 3 kPa) range. It is obvious that the

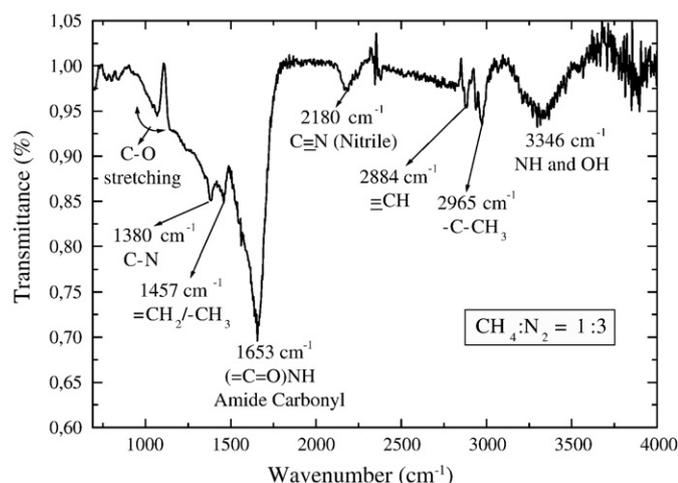


Fig. 3. A typical FTIR transmission spectra of aH-CN_x film deposited in mixture of CH₄/N₂ (1:3) at $f = 5.5$ kHz.

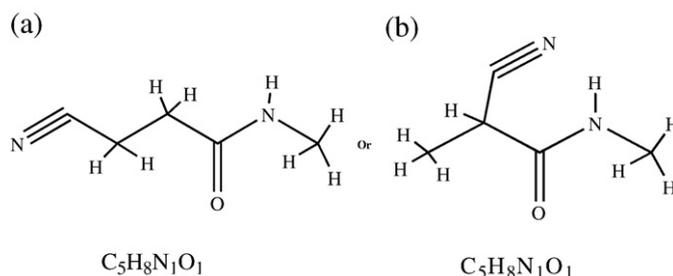


Fig. 4. The approximate empirical formula of the deposited polymer aH-CN_x film can be expressed as C_{5.2}H_{8.4}N_{1.3}(O_{0.8}), where (a) and (b) are the two possibilities by changing the nitrogen position in polymer chain.

broad band at 1560 cm⁻¹ to 1680 cm⁻¹ is attributed to amide carbonyl group (–C=O)NH and possibly weak C=N stretching band [30,31]. The absorption band observed at 1350 cm⁻¹–1480 cm⁻¹ corresponds to the C–N single stretching bond [31]. Finally, the absorption peak at 1080 cm⁻¹ to 1160 cm⁻¹ corresponds to the C–O (ketones group) stretching mode [32]. The absorption peaks appear in a regular way with different intensities in the IR spectrum. From Fig. 3, we see that the bands attributed to 1350–1480 cm⁻¹, 1560–1665 cm⁻¹ and 2100–2250 cm⁻¹ respectively, indicating the carbon and nitrogen atoms in the CN_x film are linked as C–N/CH₂ or CH₃, Amide carbonyl group (possibly weak C=N bond) and C≡N bonds.

3.3. Elemental analysis

From elemental analysis it is obtained that the composition of the film is the following (in wt.%): C: 61.8, H: 8.4, N: 17.7. After summing up these values (87.9 wt.%) it is clear that there is something more the film, not belonging to C, H, or N. This means that 12.1 wt.% of the sample belongs to one or more other elements. Due to the indications given by ¹³C MAS NMR (signal at 173 ppm, C=O bonds) and the IR vibrations discussed at about 1100 cm⁻¹ caused by the same structural unit, along with the already mentioned presence of OH groups on the surface, the existence of oxygen in the sample is suggested. A transfer of the composition given in weight percentages into a molar one allows to derive the approximate composition of this polymer aH-CN_x film as: C_{5.2}H_{8.4}N_{1.3}(O_{0.8}). Based on these above findings, Fig. 4(a and b) proposed the following examples of structural motifs for the aH-CN_x polymer film.

The broaden side bands in Fig. 1; indicate the existence of a large number of protons in the deposited film. The presence of –CH₃ groups and also non-bridged –OH groups supports the results obtained from FTIR spectroscopy. The overlapping NH and –OH band has been observed in FTIR spectrum. The ¹H and ¹³C signals are broadened due to strong homo and hetero-nuclear dipolar coupling and due to the amorphous nature of the film deposited film. For that reason we obtained few broad signal and which are not so easy to interpret. However, also surface adsorbed water molecules can give a pronounced contribution to the broad signal at about 4 ppm in addition [21,22]. On the other hand, two main signal areas can be attributed from Fig. 2, one at 173 ppm and another is slightly structured as well as broad signal between 10 ppm and 60 ppm, with an asymmetric tail in the low-field part of this signal. Due to the amorphous, disordered nature of this sample, the observed signals are broad, overlapped and only hardly to assign. Relatively low-field shifted signals cover the range of –O-CH₂–, CH-O, CH₃-N, or C-NH₂ units in the matrix. The present aH-(CN)_x film is dominated by CH₃-C or CH₃-N units giving resonances between about 10 and 40 ppm which is in contrast with previously published studies on amorphous (CN)_x films by Gammon et al. This means, carbon is mainly in the sp³ hybridized state. Due to an overlap with spinning side bands in the region at 120 ppm, a possible existence of few C@N triple bonds may be covered. Fig. 3 depicts the presence of nitrile group at 2180 cm⁻¹ and also the presence of double bond structure (C=N or C=C) at

1600 cm^{-1} which eventually support the results obtained from NMR. More over the presence of C–N in the aH-(CN)_x film is observed in both FTIR and NMR spectrum. The approximate composition of this polymer aH-CN_x film can be expressed as: C_{5.2}H_{8.4}N_{1.3}(O_{0.8}) obtained from elemental analysis.

4. Conclusions

From FTIR spectroscopy it has been obtained that the carbon and nitrogen atoms in the aH-CN_x film are mainly present as C–N, CH₂ or CH₃ at 1350–1480 cm^{-1} , and amide carbonyl groups ((=C=O)NH, including possibly weak C=N stretching bond) at 1560–1665 cm^{-1} . Furthermore, –C-CH₃ and ≡CH bands at 2884–2965 cm^{-1} , C≡N bands at 2100–2250 cm^{-1} and overlapping NH and OH bands at 3140–3500 cm^{-1} appear. These results are in agreement with findings of solid state NMR experiments indicating the dominating CH₃-C or CH₃-N groups in the matrix, accompanied by few C=O groups. Elemental analysis proposed the approximate composition of this polymer aH-CN_x film as: C_{5.2}H_{8.4}N_{1.3}(O_{0.8}).

Acknowledgements

Part of this work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich SFB/TR24 "Fundamentals of Complex plasmas", by the Federal Ministry of Educational and Research (BMBF) through Verbundprojekt "Campus PlasmaMed", and by The International Max-Planck Research School (IMPRS) "Bounded Plasmas". Dr. A. Zehl (Humboldt University) is kindly acknowledged for performing the elemental analysis. Thanks to Mr. Kaleswara Rao Basvani, Institute for Biochemistry, Inorganic Department, Greifswald, for several helpful discussions.

References

- [1] W.J. Gammon, D.J. Malyarenko, O. Kraft, G.L. Hoatson, A.C. Reilly, B.C. Holloway, *Phys. Rev. B* 66 (2002) 153402.
- [2] N. Hellgren, M.P. Johansson, E. Broitman, L. Hultman, J.E. Sundgren, *Phys. Rev. B* 59 (1999) 5162.
- [3] L. Wan, R.F. Egerton, *Thin Solid Films* 279 (1996) 34.
- [4] C. Spaeth, M. Kuhn, F. Richter, U. Falke, M. Hietschold, R. Kilper, U. Kreissig, *Diamond Relat. Mater.* 7 (1998) 1727.
- [5] S.E. Rodil, S. Muhl, *Diamond Relat. Mater.* 13 (2004) 1521.
- [6] Junying Hao, Tao Xu, Weimin Liu, *J. Non-Cryst. Solids* 351 (2005) 3671.
- [7] F. Cerny, J. Gurovie, I. Huttel, J. Suchanek, A. Djouadi, V. Hnatowicz, *Diamond Relat. Mater.* 8 (1999) 1730 (2).
- [8] J. LaManna, J. Braddock-Wilking, S.-H. Lin, B.J. Feldman, *Solid State Commun.* 109 (1999) 573.
- [9] F. Alvarez, N.M. Victoria, P. Hammer, F.L. Frire, M.C. dos-Santos, *Appl. Phys. Lett.* 73 (1998) 1652.
- [10] S. Bhattacharya, C. Vallee, C. Cardinaud, O. Chauvet, G. Turban, *J. Appl. Phys.* 85 (1999) 2162.
- [11] T. Szorenyi, E. Fogarassy, C. Fuchs, J. Hommet, F.L. Normand, *Appl. Phys., A Mater. Sci. Process.* 69 (1999) 941.
- [12] Y.H. Cheng, X.L. Qiao, J.G. Chen, Y.P. Wu, C.S. Xie, S.B. Muo, Y.B. Sun, B.K. Tay, *Appl. Phys., A Mater. Sci. Process.* 74 (2002) 225.
- [13] A. Majumdar, J. Schäfer, P. Mishra, D. Ghose, J. Meichsner, R. Hippler, *Surf. Coat. Technol.* 201 (2007) 6437.
- [14] A.Y. Liu, M.L. Cohen, *Science* 245 (1989) 841.
- [15] N. Hellgren, M.P. Johansson, B. Hjörvarsson, E. Broitman, M. Östblom, B. Liedberg, L. Hultman, J.-E. Sundgren, *J. Vac. Sci. Technol. A* 18 (2000) 2349.
- [16] S.H. Lin, J. Braddock-Wilking, B.J. Feldman, *Solid State Commun.* 114 (2000) 193.
- [17] J.C. Sanchez-Lopez, C. Donner, F. Lefebvre, C. Fernandez-Ramos, A. Fernandez, *J. Appl. Phys.* 90 (2001) 675.
- [18] L. Dong, C. Yip-Wah, Y. Shengtian, W. Ming-Show, F. Adibi, W.D. Sproul, *J. Vac. Sci. Technol. A* 12 (1994) 1470.
- [19] A. Majumdar, R. Hippler, *Rev. Sci. Instrum.* 78 (2007) 075103.
- [20] A. Majumdar, J.F. Behnke, R. Hippler, K. Matyash, R. Schneider, *J. Phys. Chem. A* 109 (2005) 9371.
- [21] D.G. Cory, W.M. Ritchey, *J. Magn. Res.* 80 (1988) 128.
- [22] G. Scholz, G. Dörfel, I. Heidemann, D. Feist, M.R. Stösser, *J. Solid State Chem.* 179 (2006) 1119.
- [23] W.J. Gammon, G.L. Hoatson, B.C. Holloway, R.L. Vold, A.C. Reilly, *Phys. Rev. B* 68 (2003) 195401.
- [24] A.D. Graaf, G. Dinescu, J.L. Longueville, M.C.M. Sandan, D.C. Schram, E.H.A. Dekempeneer, L.J.V. Ijzendoorn, *Thin Solid Films* 333 (1998) 29.
- [25] A. Zocco, A. Perrone, A. Luches, R. Rella, A. Klini, I. Zergioti, C. Fotakis, *Thin Solid Films* 349 (1999) 100.
- [26] T. Heitz, B. Drevillon, C. Godet, J.E. Bouree, *Phys. Rev. B* 58 (1998) 13957.
- [27] D. Li, Y.W. Chung, S. Yang, M.S. Wong, F. Adibi, W.D. Sproul, *J. Vac. Sci. Technol. A* 12 (1994) 1470.
- [28] J.H. Kaufman, S. Metin, D.D. Saperstein, *Phys. Rev. B* 39 (1989) 13053.
- [29] T. Bezrodna, G. Puchkovska, V. Shymanovska, J. Baran, H. Ratajczak, *J. Mol. Struct.* 700 (2004) 175.
- [30] H. Günzler, Hans-Ulrich Gremlich, *IR Spectroscopy*, WILEY-VCH Verlag GmbH, 69469 Weinheim (Federal Republic of Germany), 2002.
- [31] T. Szorenyi, C. Fuchs, E. Fogarassy, J. Hommet, F.L. Normand, *Surf. Coat. Technol.* 125 (2000) 308.
- [32] Z.M. Ren, P.N. Wang, Y.C. Du, Z.F. Ying, F.M. Li, *Appl. Phys., A Mater. Sci. Process.* 65 (1997) 407.
- [33] Abhijit Majumdar, Karsten Schröder, Rainer Hippler, *J. Appl. Phys.* 104 (2008) 074702.