

FTIR investigations on X-N bonds of annealed PolySi/NIDOS films

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Abstract

The paper presents Fourier transform infrared spectroscopy investigations on composition bonds of polysilicon/Nitrogen Doped Silicon PolySi/NIDOS film deposited by Low Pressure Chemical Vapor Deposition or (LPCVD). These films are annealed at 700°C for different duration from 15 min to 480 min. The FTIR results indicate the presence Si-N, BN and B-N-B bonds located at different wavenumber. The decomposition results show the existence of more complex c-BN and h-BN peaks. In addition, The FTIR spectra of polySi/NIDOS films annealed at different durations are used to calculate bond densities of Si-N, B-N-B, h-BN and c-BN. Moreover, after 60 min the films are dense by c-BN and h-BN complexes. The strong concentration of these complexes keeps the boron penetration in dioxide layer which improve MOSFET component.

Keywords: FTIR, BN complex, density, boron, nitrogen.

1. Introduction

The excellent physical and chemical properties of the boron nitride (BN) make this compound an attractive material in the last 10 years [1-3]. In particular BN exhibits extremely high hardness, high electrical insulation, and good thermal conductivity and parallels the crystalline structure [4-6]. The main aim of these researches is to improve of the polysilicon gate MOSFET structures by reducing the doped penetration in oxide layer [7, 10]. For this we added new layer between oxide and polysilicon layers. Nitrogen Doped Silicon NIDOS layer is obtained by mixture disilane and ammonia, in order to obtain X-N bonds and create insulator layer [11-14].

In order to improve the oxide quality of MOS component, the authors in the present work study Fourier transform infrared spectroscopy investigations on X-N bilayer films polySi/NIDOS annealed at 700°C for different durations.

2. Experiments

Using low pressure chemical vapor deposition (LPCVD) method two polysilicon layers are deposited on oxidized single crystal silicon substrates (P-type, 25-n-oxide thick).

The first layer deposited from disilane (Si_2H_6) and ammonia (NH_3) (about 200-n-thick), was in-situ nitrogen doped. On this later, a second polysilicon layer deposited by the disilane and boron trichloride (BCl_3) was also in-situ boron doped (about 130-n-thick).

Finally the samples were thermally annealed at 700°C for different duration. (See Fig. 1).

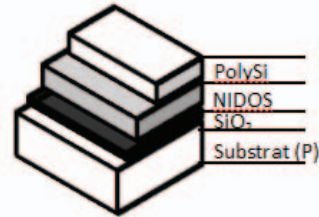


Fig.1 Sample structure.

3. FTIR results

Figure 2 shows the IR transmittance spectra recorded between 400 and 4000 cm^{-1} of the polySi/NIDOS/ SiO_2 /Si films. These films are annealed at 700°C for different duration between 15min and 480min.

We note that the signification transmittance peaks are located between 600 and 1500 cm^{-1} . In what follows, we will make a detailed study on this wavelength see figure 3.

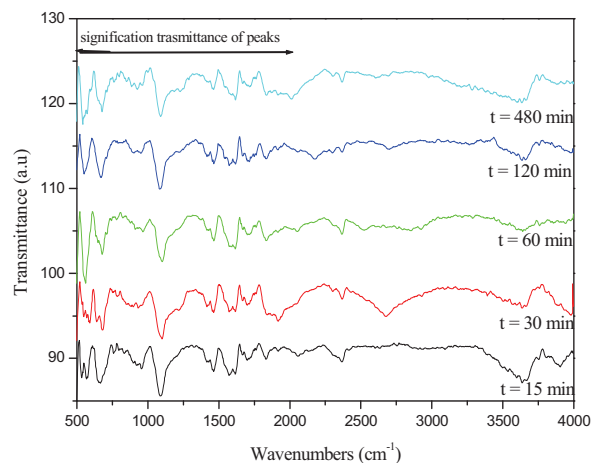


Fig. 2 IR transmittance spectra recorded between 400 and 4000 cm^{-1} of the polySi/NIDOS/ SiO_2 /Si films.

Figure 3 show the IR transmittance spectra recorded between 1500 cm^{-1} and 600 cm^{-1} .

The FTIR obtained results show the appearance of several bands detected in the material.

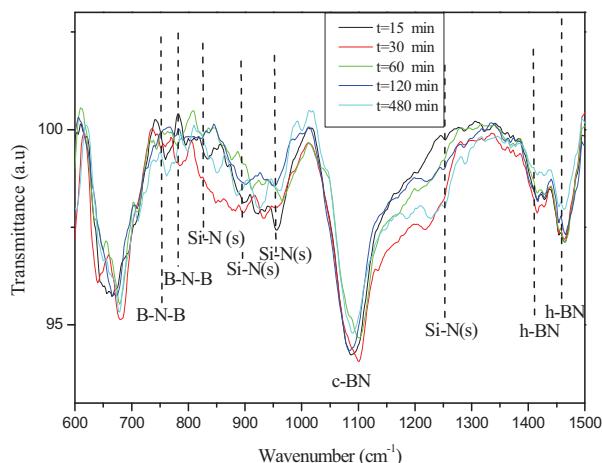


Fig. 3 The principal peaks appear in the wave number located between 600cm⁻¹ and 1500cm⁻¹ for PolySi/NIDOS films.

We noticed that the peaks detected in the films are nitrogen type (X-N) as Si-N and BN. The peaks located around 1083 cm⁻¹ assigned to cubic c-BN bond [15-17] and the bands positioned at 1400 and 626 cm⁻¹ were assigned to hexagonal h-BN [18-20]. Moreover, the peaks situated at 950, 850, 480 and 830 cm⁻¹ were assigned to stretching vibration mode Si-N (s) [21-23].

For our study, we focus on the domain 800-1350 cm⁻¹. This wide strip was divided into different Gaussian peaks (figure 4-6) corresponding to the following bond (see table 1).

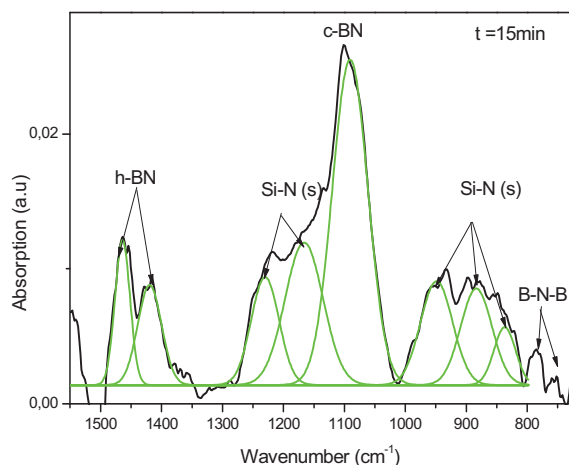


Fig. 4 Deconvolution of the absorbance band located between 1500 and 750 cm⁻¹ for 15 min.

The deconvolution results show, appearance of different kinds of peaks Si-N, B-N-B, h-BN and c-BN detected to 15 from 60min, we notice, the same bonds were found for durations 120 and 480 min [19]. In addition, the absorbance intensity of the c-BN peak is two to three times greater than the Si-N bond according annealing time.

The objective of this work is to calculate the density of each bond in the films polySi/NIDOS for different annealing times,

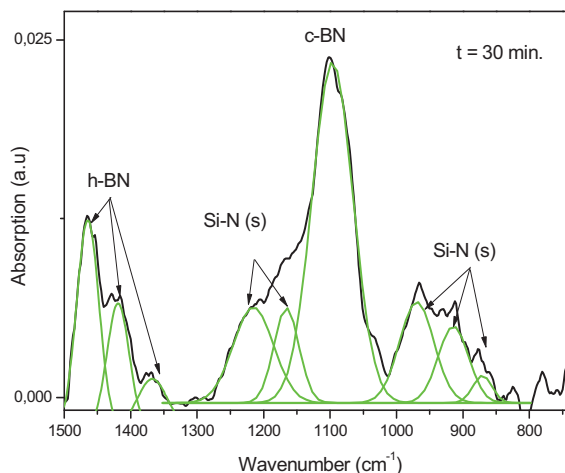


Fig. 5 Deconvolution of the absorbance band located between 1500 and 750 cm⁻¹ for 30 min.

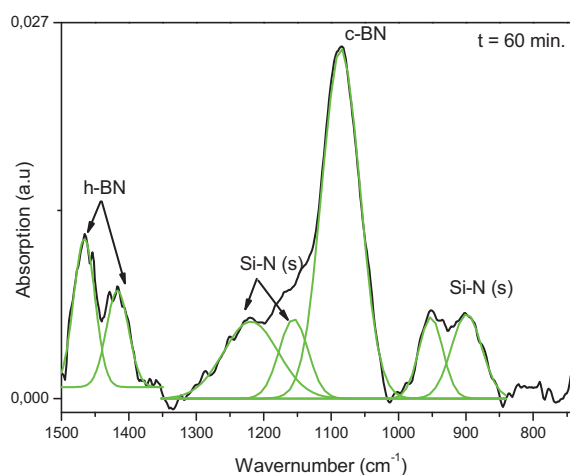


Fig. 6 Deconvolution of the absorbance band located between 1500 and 750 cm⁻¹ for 60 min.

Table 1: Wavenumbers for different bonds detected

Bond	Wavenumber	References
Si-N	840,860,890,950,1250,1150	[21-23]
c-BN	1080	[15-17]
h-BN	1400, 1390, 1500	[18-20]
B-N-B	735, 750, 811, 790	[17], [20] [23]

in order to optimize annealing condition. In what follows, we will calculate the quantitative density of each link. This calculation is based on decomposition band

The infrared absorption spectroscopy can not only identify the vibrant connections but also to determine the concentration. Based on the Lorentz model that considers the solid as a set of oscillators, we can correlate the area of a characteristic absorption band in conjunction with the concentration (or density) of this bond, using the following relationship [24].

3.1 Densities of the Si–N bonds:

In the literature, the integrated absorptions of IR active bands have been utilized for a quantitative determination; the densities of the Si–N bonds were estimated from their stretching vibration mode, using the following expression [25]

$$N_{Si-N} = K_{Si-N} \int \frac{\alpha(\omega)}{\omega} d\omega \quad (1)$$

Where: N_{Si-N} the density of the Si–N bonds, K is a proportionality coefficient linked to the bond oscillator force, $\alpha(\omega)$ the absorption coefficient at the wavenumber ω .

This equation can be given function of the area of the bond:

$$N_{Si-N} = K_{Si-N} \frac{A_{Si-N}}{\omega} \quad (2)$$

Where A_{Si-N} the area of bonds and the value of the proportionality coefficient $K_{Si-N} = 6.30 \times 10^{18} \text{ cm}^{-2}$ [26] were used to calculate the bond densities

3.2. Densities of the h-BN, c-BN and B-N-B bonds:

According S. Jäger and all, the oscillator concentration of N_i , can be calculated from the integrated absorption using almost the same equation 1, except the calibration constant A which relates the strength of the absorption mode to the concentration of the corresponding element:

$$N_i = A_i \int \frac{\alpha(\omega)}{\omega} \quad (3)$$

$A_{h-BN} = 1, 71 \cdot 10^{19} \text{ cm}^{-2}$, $A_{B-N-B} = 9, 1 \cdot 10^{19} \text{ cm}^{-2}$ and $A_{c-BN} = 1, 26 \cdot 10^{19} \text{ cm}^{-2}$ [23].

The figure 5 shows the calculated bond densities of the Si–N, B–N–B, h–BN and c–BN bonds at 700°C for 15, 30, 60, 120 and 480 min.

We observe, The B–N–B and Si–N densities bond decreased according time increased. On the other hand, the c–BN and h–BN bond densities increased according time. The results indicate that the decrease of B–N–B and Si–N densities encourages the formation of the h–BN and c–BN bonds in the films, this explained the densities augmentation.

In addition, we note that after 60 minutes the film will be dense by c–BN and h–BN bond, the c–BN bond is twice as dense than h–BN which make the stability of the film.

The formation of the complex cubic boron nitride (c–BN) which exhibits a peculiarity in her physical and chemical properties (hardness, high thermal conductivity, transparency) and its higher chemical stability and lower reactivity at high temperatures [28] reduce effectively the boron diffusion in the SiO₂ layer by azote presence. This result is in good concordance by Chao and all [29].

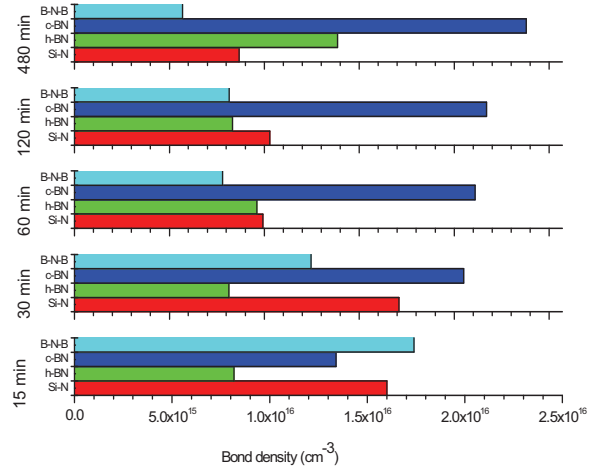


Fig. 7 Bond densities of films annealed at 700°C at different duration.

4. Conclusion

FTIR analysis investigations on h–BN and c–BN bilayer films deposited by LPCVD have been presented. The films are annealed at 700°C from different duration from 15min to 480 min. the transmittance spectra film confirm the presence of diverse azote peaks. The decomposition of these bonds shows the presence of more peaks and specially the cubic and hexagonal BN bond. The bands densities calculated confirmed that after 700°C/60 min the films will denser by the c–BN, it is a barrier to the boron diffusion [27, 28]. Finally, the polySi/NIDOS structure can be used as gate in micro technology applications.

5. References

- [1] M. Monajjemi, M. Seyed Hosseini and F. Molaamin, "Theoretical Study of Boron Nitride Nanotubes with Armchair Forms", *Taylor & Francis Group, Fullerenes, Nanotubes, and Carbon Nanostructures*, vol. 21, pp 381–393, 2013.
- [2] L. M. GAMEZA, "Peculiarities of spontaneous crystallization of cubic boron nitride single crystal powders in the Li–B–N (H, Be) system", *Taylor & Francis Group, High Pressure Research: An International Journal*, Vol.18, pp. 373–378, 2000.
- [3] S. Ohtani, T. Yano, S. Kondo, Y.Kohno, Y. Tomita, Y. Maeda, K.Kobayashi. "Electron emission from h–BN films codoped with Mg and O atoms", *Thin Solid Films*, 2013.
- [4] K. Yamamoto, M. Keunecke, K. Bewilogua, Zs. Czigany, L. Hultman. "Structural features of thick c–boron nitride coatings deposited via a graded B–C–N interlayer". *Elsevier Science, Surface and Coatings Technology*. Vol 142–144, pp. 881–888, 2001.
- [5] M.I. Petrescu, M-Gabriela Balint. "Structure and properties modifications in boron nitride. Part I: direct polymorphic transformations mechanisms". *U.P.B. Sci. Bull., Series B*, Vol. 69, No. 1, 2007.

- [6] T. Zhang, M. Wu A, S. Zhang, J.Wang , D. Zhang, F. He, Z. Li. "High temperature dielectric loss of h-BN at X band and its dependence on the electron structure, defects and impurities". *Solid State Sciences*, vol. 12, pp.1599-1602, 2010.
- [7] R. Mahamdi, L.Saci, F. Mansour, P. Temple-Boyer, E. Scheid and L. Jalabert. "Physicochemical characterization of annealed polySi/NIDOS/SiO₂ structures". *Spectroscopy Letters*. Vol. 42, N°3. (2009), pp.167-170. ISSN (print):0038-7010/ ISSN (online): 1532-2289.
- [8] Lynda Saci, Ramdane Mahamdi, Farida Mansour, Jonathan Boucher, Maeva Collet, Elena Bedel Pereira, and Pierre Temple-Boyer. "Study of Nitrogen Effect on the Boron Diffusion during Heat Treatment in Polycrystalline Silicon/Nitrogen-Doped Silicon Thin Films" *Japanese Journal of Applied Physics*, Vol. 50, (2011), pp. 051301 1-5. ISSN (print) 0021-4922, ISSN (online) 1347-4065.
- [9] T. Yamamoto, K. Okabe, T. Kubo, K. Goto, H. Morioka, Y. Wang, T. Lin, S. Talwar, M. Kase , T. Sugii, "Novel polysilicon gate engineering with a laser thermal process for sub-40 nm CMOS devices", *Solid-State Electronics*, vol. 48, pp. 1837–1842, 2004.
- [10] T. Afentakis , M. Hatalis, "A simple analytical model for the dependence of the propagation delay of the polycrystalline silicon inverter on temperature", *Solid-State Electronics*, vol. 46, pp. 2301–2306, 2002.
- [11] Lynda Saci, Ramdane Mahamdi, Farida Mansour and Pierre Temple-Boyer. "Experimental study of the boron redistribution in two series of bilayer films silicon-based". *Istanbul University - Journal of Electrical and Electronics Engineering (IU-JEEE)*. ISSUE 23, volume 12 (1), 2012, pp.1453-1456
- [12] Lynda Saci, Ramdane Mahamdi, Farida Mansour, Jonathan Boucher, Maeva Collet, Elena Bedel Pereira, and Pierre Temple-Boyer. "Study of Nitrogen Effect on the Boron Diffusion during Heat Treatment in Polycrystalline Silicon/Nitrogen-Doped Silicon Thin Films" *Japanese Journal of Applied Physics*, Vol. 50, (2011), 051301(5 pages).
- [13] R. Mahamdi, F. Mansour, H. Bouridah, P. Temple-Boyer, E. Scheid, L. Jalabert. "Nitrogen doped silicon films heavily boron implanted for MOS structures: Simulation and characterization". *Materials Science in Semiconductor Processing*, Vol.N°13, pp.383–388 2010
- [14] R. Mahamdi, L.Saci, F. Mansour, P. Temple-Boyer, E. Scheid and L. Jalabert. "Physicochemical characterization of annealed polySi/NIDOS/SiO₂ structures". *Spectroscopy Letters*. Vol. 42, N°3. (2009), pp.167-170
- [15] A. Essafti, E. Ech-chamikh and J.L.G. Fierro. "Structural and chemical analysis of amorphous B-N-C thin films deposited by RF sputtering" *Diamond and related materials*, Vol. 14, 2005, pp. 1663-1668.
- [16] A. Essafti, C. Gomez-Aleixander, J.L.G. Fierro. M. Fernandez and J. M. Albella. "Chemical vapor deposition synthesis and characterization of co-deposited silicon-nitrogen-boron materials", *Journal of materials research*, vol. 11, No. 10, pp. 2565-2574, Oct 1996.
- [17] M. W. Mortensen, P. G. Sorensen, O. Bjorkdahl, M. R. Jensen. H. J. G. Gundersen and T. Bjornholm, "Preparation and characterization of boron carbide nanoparticles for use as a novel agent in T cell-guided boron neutron capture therapy", *Applied Radiation and Isotopes*, vol. 64, pp. 315-324, 2006.
- [18] L. Chen, M. Huang, T. Luo, Y. Gu, L. Shi, Z. Yang, Y. Qian, "A low-temperature route to nanocrystalline boron nitride whiskers and flakes", *Materials Letters*, vol. 58, pp.3634–3636, 2004.
- [19] K. Nakamura and T. Sasaki, "Preparation of SiBN films deposited by MOCVD", *Journal of Solid State Chemistry*. Vol. 177, pp. 542–546, 2004.
- [20] Giovanni A. Battiston , Davide Berto , Annalisa Convertino , Dario Emiliani , Albert Figueras , Rosalba Gerbasi , Sesto Viticoli, "PECVD of h-BN and c-BN films from boranedimethylamine as a single source precursor", *Electrochimica Acta*, vol. 50, pp. 4600–4604, 2005.
- [21] X.W.Zhang, H.-G. Boyen, H. Yin, P. Ziemann, F. Banhart, "Microstructure of the intermediate turbostratic boron nitride layer", *Diamond & Related Materials*, vol. 14, pp. 1474–1481, 2005.
- [22] C.Y. Chan, S. Eyhusen , X.M. Meng , I. Bello , S.T. Lee , C. Ronning , H. Hofsa'ss , "The effect of substrate surface roughness on the nucleation of cubic boron nitride films", *Diamond & Related Materials*, vol. 15, pp. 55–60, 2006.
- [23] H.Fang, K.S.Krisch, B.J.Gross, C.Sodini, J.Chung, and D. Antoniadis."Low temperature furnace-grown deoxidised nitrated oxide gate dielectrics as a barrier to boron penetration". *IEEE Electron Device Lett.*, vol.13, pp.217-219, 1992.
- [24] F. Rebib, E. Tomasella, M. Dubois, J. Cellier, T. Sauvage, M. Jacquet. "SiOxNy thin films deposited by reactive sputtering: Process study and structural characterisation". *Thin Solid Films*, vol. 515, pp 3480–3487, 2007.
- [25] M.H. Brodsky, M. Cardona, J.J. Cuomo. "Infrared and Raman spectra of the silicon-hydrogen bonds in amorphous silicon prepared by glow discharge and sputtering". *Phys. Rev.*, B. Vol. 16, pp. 3556-3571, 1977.
- [26] E. Bustarret, M. Bensouda, M.C. Habrard, J.C. Bruyère. "Configurational statistics in a-SixNyHz alloys: A quantitative bonding analysis". *Phys. Rev.* vol.38, pp.8171-8184, 1988.
- [27] S. Jaiger, K. Bewilogua and C.-P. Klages. "Infrared spectroscopic investigations on h-BN and mixed h/c-BN thin films". *Thin Solid Films*, Vol. 245, pp.50-54, 1994.
- [28] J.L.P. Castineir, J.R. Leite, L.M.R. Scolfaro, R. Enderlein, H.W. Leite Alves and Jose L.A. Alves. "Stability of native defects in cubic boron nitride". *Radiation Effects & defects in Solids*, Vol. 146, pp. 49-63, 1998.
- [29] T. S. Chao, M. C. Liaw, C. H. Chu and C. Y. Chang. "Mechanism of nitrogen coimplant for suppressing boron penetration in p+ polycrystalline silicon gate of p+ metal-oxide semiconductor field effect transistor". *J. Appl. Phys.* Vol.69, pp. 1781-1783, 1996.