Imaging of SiCN thin films on silicon substrate in the scanning low energy electron microscope

Jitka Zobačová,[1*)] Erwin Hüger[2], Michal Urbánek[1], Josef Polčák[3] and Luděk Frank[1]

[1] Institute of Scientific Instruments AS CR, Královopolská 147, CZ-612 64 Brno, Czech Republic (http://www.isibrno.cz; *) e-mail: zobacova@isibrno.cz)
[2] Institute of Metalurgy, Department of Thermochemistry and Microkinetics, Clausthal University of Technology, Robert Koch- Straße 42, 38 678 Clausthal Zellerfeld, Germany
[3] Institute of Physical Engineering, Brno University of Technology, Technická 2896/2, CZ-616 69 Brno, Czech Republic (http://www.vutbr.cz)

Introduction

The Si- C- N materials have been attracting growing interest due to their excellent physical properties. They are hard, possess a large band gap, resist harsh and high temperature environments, and exhibit interesting nanostructures such as turbostratic-carbon and nanopores [1, 2, 3]. Their range of application includes anti-erosive turbines and cutting tools, opto-electronic materials, sensors, and special drug delivery pharmaceutical products [1, 2, 3]. Most of their interesting properties stems from carbon-nitrogen bonds. Hence, Si-C-N materials with a high content of carbon and nitrogen are of interest. Up to date, the highest carbon and nitrogen content could be synthesised in SiC_2N_4 and Si_2CN_4. Both chemical compositions are stable and possess the highest achieved carbon-nitrogen bond. Two different nitride bonding configuration was measured to be present.

Specimen

Silicon nitride (Si_3N_4) tetragons are joined together by carbon-nitride bonds (-N=C=N-, carbodiimide) (see **Fig. 1**) [1, 2, 3]. Only hetero-nuclear bonds are existent [1, 2, 3]. Although carbon and silicon possess the same number of valence electrons, they bond differently to nitrogen due to their different natural bond affinity. Carbon atoms, the basics of Life, have the affinity to bond in a polymer-like fashion with hydrogen, oxygen and nitrogen. In Si-C-N carbon bonds to nitrogen also in a linear atomic arrangement (-N=C=N-). On the other hand, silicon has not the capability to create Life, i.e. polymer-like bonds with hydrogen, oxygen and nitrogen. Silicon atoms remain the basics of (electronic) technology. Silicon bonds in a tetragonal fashion with oxygen and nitrogen which enable the growth of dense bulk materials. The peculiarity of Si-C-N lies in the combination of linear bonds N=C=N- with tetragonal bonds (Si_3N_4) to a 3-dimensional amorphous network.

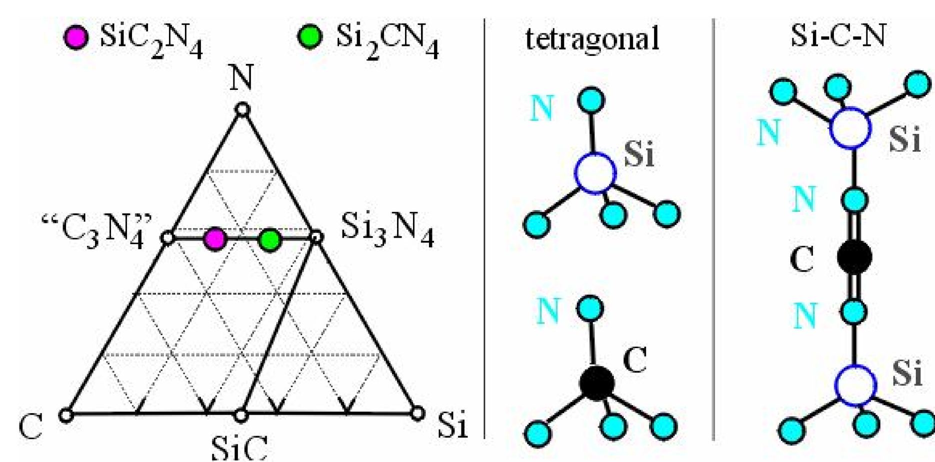

Figure 1 Phase diagram- concentration triangle (left panel), units of tetragonal bonds (middle panel) and a unit of the Si-C-N bonding configuration (right panel).

Methods

The examination of as-deposited thin films Si_2CN_4 and SiC_2N_4 on Si substrates was performed with use of low energy electron microscopy and atomic force microscopy. The SEM Vega TS 5130MM with standard vacuum conditions, equipped with the cathode lens (CL) with minimum realignment of the column [4], was used to examine the surface of uncoated, non conductive films at optimum electron energy of minimized charging up phenomena [5, 6].

Let us briefly explain the formation of surface charges of both signs at various landing energies during investigation of non - conductive thin films in low energy electron microscope. For most specimens the dependence of the total electron yield on electron landing energy σ (E) crosses two times the unit level. The minimum charging energy, the so called critical energy, is given by the intersection of the curve σ (E) with unit level. The critical energy E^{II} corresponds to the second crossover and ranges between 0,55 and 4 keV for most selection of insulators [7].

In **Fig. 2** one can see the energy dependence of the total electron emission. The probe, thin Si_2CN_4 film, is bombarded by incident electrons at beam energy E_L. The areas of positive and negative charging are indicated. The specimen is placed in vacuum in a region free of external electric fields. The slow secondary electrons (SE) are re- attracted by the positively biased surface. The resulting recaptured current decreases efficiently the SE yield. The charge equilibrium at a much lower surface potential $U_S^{(3)}$ is reached at point D.

Results : the LESEM and AFM analyse

Notice the micrographs of positively charged Si_2CN_4 film at E_L = 1,8 keV (left), uncharged at critical energy E^{II} = 3,8 keV (middle) and slightly negatively charged at E_L = 5,2 keV (right). In **Fig. 3** the micrographs of positively charged SiC_2N_4 film at E_L = 1,1 keV (left), almost uncharged at critical energy E^{II} = 2,1 keV (middle) and negatively charged at E_L = 3,1 keV (right) are obvious. The optimum energy for imaging of Si_2CN_4 and SiC_2N_4 thin films is different. Finally, in **Fig. 4** and **Fig. 5** we can see LESEM micrographs of the structure of both investigated films at critical energy and the results of topography of both investigated thin films measured by Atomic Force Microscope type Pacific Nanotechnology Nano-R in contact mode.

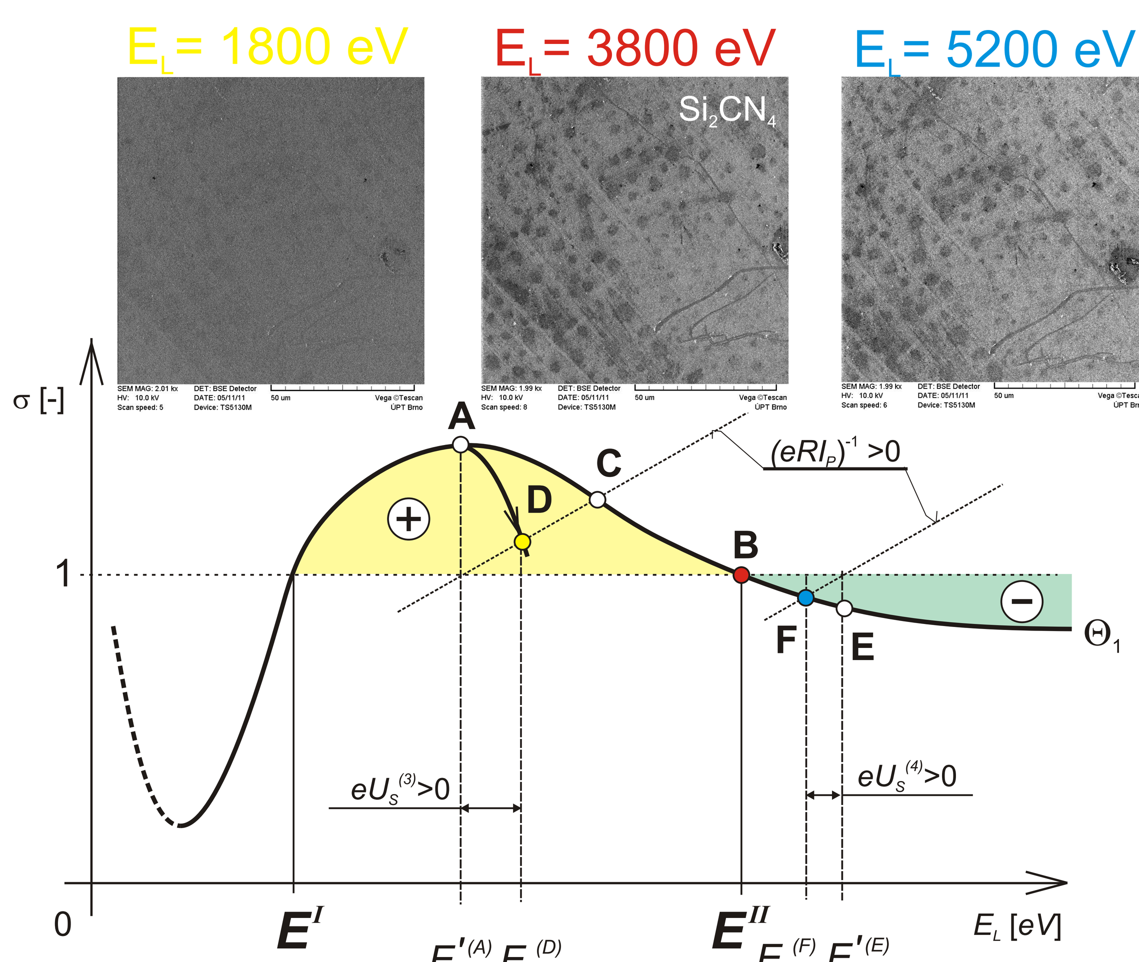

Figure 2 The energy dependence of the total electron emission. The Si_2CN_4 thin film in vacuum is bombarded by incident electrons at energy E_L. The areas of positive and negative charging are indicated.

Conclusion

The experiments performed in low energy scanning electron microscope have confirmed that the optimum electron energy for investigation of thin SiCN films does exist and is different for Si_2CN_4 and SiC_2N_4 thin films. The possible explanation is the different thickness of both films and differences in the structure concerning the presence of covalent C-N bonds. The hypothetical explanation deals with larger amount of nanopores (mesoporous) in SiC_2N_4 compared to the Si_2CN_4 film. The oxidation of nanopores converts the pore-walls into SiO_2 pore-walls. Further investigations are necessary to bring the answer to question: Can the existence of nanopores (or the SiO_2 of the pore-walls) affect the charging effect? In this favourable case, the microscopy at optimum electron energy brings better results than low electron energy in general.

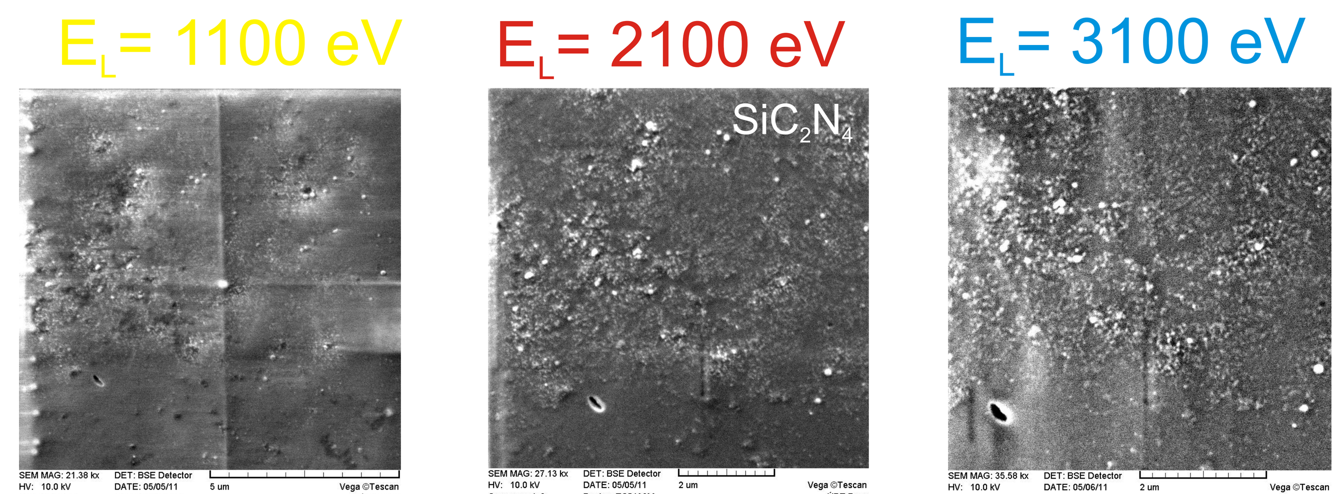

Figure 3 The micrographs of positively charged SiC_2N_4 film at E_L = 1,1 keV (left), almost uncharged at critical energy E^{II} = 2,1 keV (middle) and negatively charged at E_L = 3,1 keV (right).

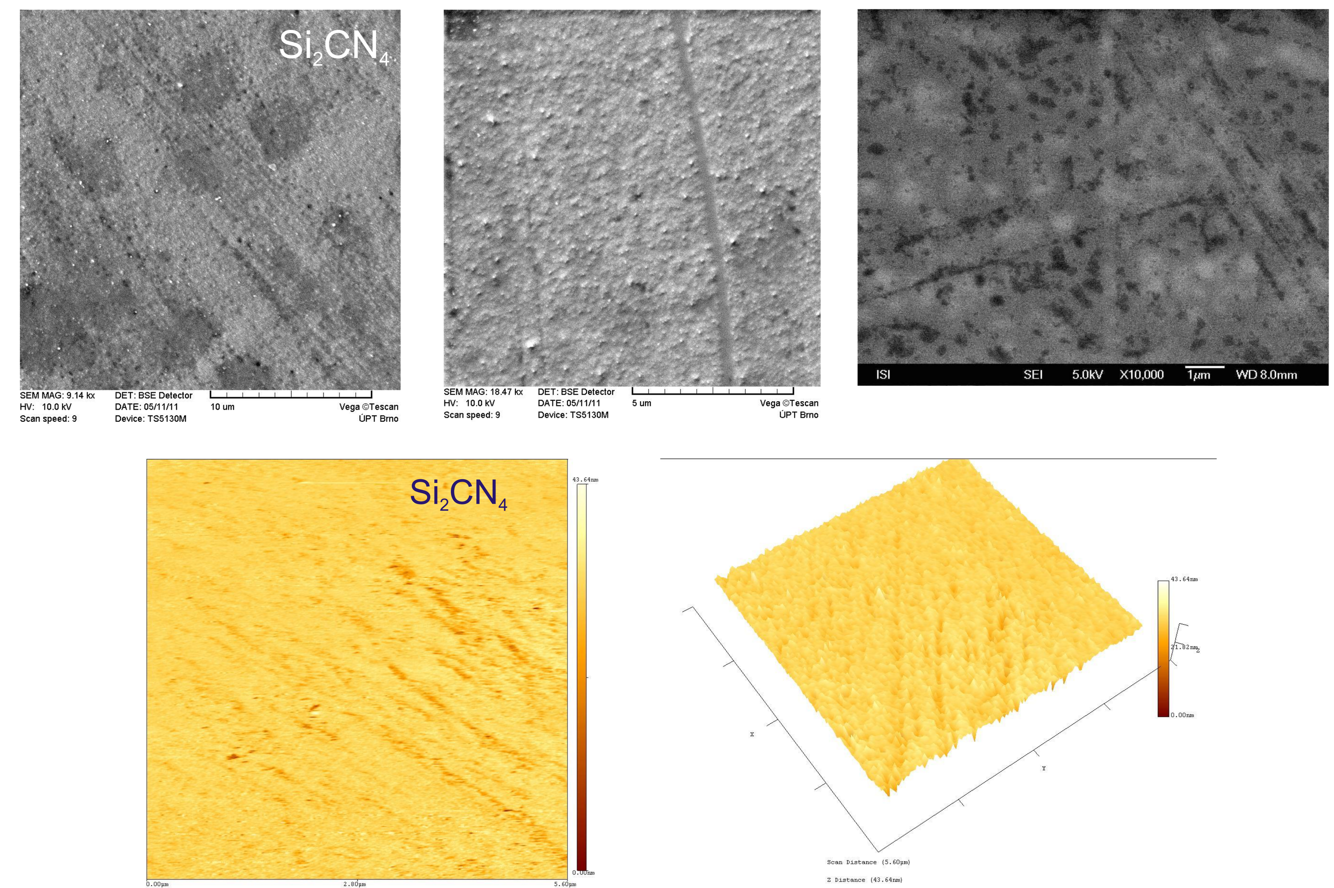

Figure 4 The micrographs of Si_2CN_4 film at critical energy E^{II} = 3,8 keV (upper row, left and middle), the SE image of the same specimen at 5 keV (upper row, right) and AFM topography of another spot on the same specimen with the scan size of 5,6×5,6 μm, z range equal to 43 nm (lower row). Courtesy to A. Rek and F. Mika for the micrograph in microscope JEOL JSM 6700F.

Figure 5 The micrographs of SiC_2N_4 film at critical energy E^{II} = 2,1 keV (left) and AFM topography of another spot on the same specimen with the scan size of 2,1×2,1 μm, z range equal to 13 nm (middle and right).

References

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Results: the XPS analyse

The amorphous Si_2CN_4 film of 2 μm thickness and SiC_2N_4 film of 1 μm thickness were magnetron sputter deposited on Si substrates at the Karlsruher Institute of Technology (KIT) [1,2,3] in Germany. Before the XPS and microscopy investigation the SiO_2 layer was removed from the surface of thin films. The probes were soaked to buffer solution with F ions with constant value of PH and with etching velocity 80 nm /min and centrifuged for 10 s in the case of Si_2CN_4 and for 40 s for SiC_2N_4 , respectively. According to the results from FTIR, RBS, XRR and AES measurement [3], the thickness of SiO_2 layer ranged from 2 to 40 nm. The X ray photoelectron spectroscopy scans of N (1s), C (1s) and Si (2p) core level peaks in **Fig. 6** revealed C=N as well as C-N and Si-N bonds. The Si - C bond was not detected for these SiCN films prepared by magnetron sputtered deposition techniques. The XPS instrument is equipped with rtg source Omicron with Al anode (1486,6 eV) and hemispherical analyzer.

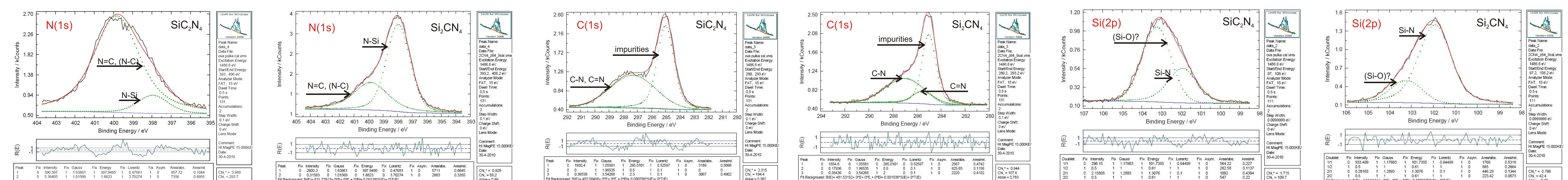

Figure 6 The core- level-shifts to hetero bonds identification. The comparison of high resolution X ray photoelectron spectroscopy scans of N(1s), C(1s) and Si (2p) peaks done for SiC_2N_4 and Si_2CN_4.