

**Резюмета на публикациите на доц. дФн Корнели Григоров след заемане на  
научната длъжност доцент**

1. K.Grigorov, V.Tsaneva, A.Spasov, W.Matz, R.Groetzschel, "RBS and ion channeling study of YBCO/STO and YBCO/LSMO/STO structures. Oxygen content estimated by X-ray diffraction", *Vacuum* **69** (2003) 315-319.

**Abstract:** The structure and the elemental depth distributions of Y1Ba2Cu3O7-d (YBCO) and La0.7Sr0.3MnO3 (LSMO) were examined by  $\theta$ -2 $\theta$  XRD, and by 1.7MeV 4He+ Rutherford Backscattering Spectrometry (RBS) in random and channeling geometry. The YBCO layers were magnetron sputtered, with the varying parameters oxygen pressure and annealing time. The layers have high crystalline quality and an almost sharp interface with the substrate as revealed by the analysis. It is shown that the oxygen content influences considerably not only the superconducting behavior, but also the lattice parameters and the  $\chi_{\min}$  parameter (the minimum yield that is the ratio of aligned to random Rutherford backscattering spectra). We have found by high-precision RBS simulation that, independent on the film quality, a disordered interface region of 20–30nm is present in all structures. As a complementary study we have performed also AES depth profiling.

2. G.Beshkov, T.Radev, V.Bakardjieva, H.S.Maciel, K.Grigorov, "Characterization of PECVD – silicon nitride passivation films after Rapid Thermal Annealing", *26 Workshop on Compound Semiconductor Devices and Integrated Circuits held in Europe, WOCSDICE, 2002*.

**Abstract:** We have studied the influence of the Rapid Thermal Annealing (RTA) process on the hydrogen incorporation, (Si-H and N-H bonds), in Si<sub>x</sub>N<sub>y</sub> passivation layers obtained by Plasma enhanced chemical vapor deposition (PECVD). Depending on the bonding configuration (Si-N or NH), hydrogen can increase the wet etching rate, change the electrical properties, increase the residual stress and as consequence to decrease the thermal stability of the compound. N-H bonds, in general are responsible for the compressive stress of the S<sub>3</sub>N<sub>4</sub> films [1]. Concerning the interface state density of the system S<sub>3</sub>N<sub>4</sub> deposited onto n-GaN, recent paper appeared [2] dealing with PECVD of Si<sub>3</sub>N<sub>4</sub> · films. Subject of other works are the properties of the silicon-nitride films deposited by different techniques, such as ECR [3], LPCVD, PECVD. APCVD [4,5].

3. G.Beshkov, V.Krastev, K.Grigorov, H.Maciel, Ting-Ao-Tang, Veining Huang, "X-Ray photoelectron spectroscopy study of phosphorus silicate glasses", *Surface & Coatings Technology*, **161**, 2002 11-19.

**Abstract:** Samples of phosphorus silicate glass (PSG) layers were deposited in a class 100 clean room in two kinds of industrial type reactors: by plasma enhanced chemical vapor deposition (PECVD) and micro pressure chemical vapor deposition ( $\mu$ PCVD) at working temperatures of 380°C and 430°C, respectively. After deposition the samples were subjected to rapid thermal annealing (RTA) in a vacuum at 5=10  $\mu$ Pa and temperatures of 800°C, 1000°C, 1200°C and 1400°C for 15–180 s. X-Ray photoelectron spectroscopy (XPS) investigations show that phosphorous oxides pass through a phase transition and evaporate, while silicon oxides evaporate and decompose. The rate of etching in 'p' etcher of  $\mu$  PCVD-PSG layer before annealing is 1023  $\text{\AA} \text{ min}^{-1}$ , after RTA at 800 °C for 15 s it is 909  $\text{\AA} \text{ min}^{-1}$ , and after annealing for 3 min it is 690  $\text{\AA} \text{ min}^{-1}$ . In the case of RTA at 1000, 1200 and 1400°C for 3 min the etching rates are 660, 469 and 351  $\text{\AA} \text{ min}^{-1}$ , respectively, i.e. RTA results in considerable decrease of rate of etching. The same behavior

shows curves related to PSG layers obtained by PECVD. IR spectra show that P=O bond vibration at  $1320\text{ cm}^{-1}$  appears at temperatures of annealing  $T \geq 1000^\circ\text{C}$  and time interval 60–180 s. A correlation between PSG layers characteristics and conditions of RTA is found.

4. M.Massi, J.M.Ocampo, H.S.Maciel, K.Grigorov, C. Otani, L.V.Santos, R.D.Mansano, “Plasma etching of DLC films for micro-fluidic channels” **Microelectronics Journal** **34** (2003) 635-638.

**Abstract:** The goal of this work is to study the effect of plasma etching process on the surface properties of diamond-like carbon thin films having in mind the applicability of this material for construction of microfluidic channels. The films were deposited by dc magnetron sputtering onto p-type (100) 3 in. silicon wafers, at a deposition rate of 8 nm/min. The etch processes have been carried out in a RIE reactor with the discharge produced in an atmosphere of oxygen diluted in argon. Oxygen contents varied from 0 to 100% and different values of the power discharge (from 20 up to 150 W) have been applied. The surface roughness and wall profiles were examined by atomic force microscopy and scanning electron microscopy in order to verify the quality of the final surface obtained after etching.

5. J.Libardi, K.Grigorov, M.Massi, C.Otani, S.P.Ravagnani, H.S.Maciel, M.Guerino, J.M. Ocampo, “Comparative studies of the feed gas composition effect on the characteristics of DLC films deposited by magnetron sputtering”, **Thin Solid Films** 459, (1-2), pp. 282-285.

**Abstract:** Mixtures of acetylene/argon and methane/argon with different volume percents of hydrocarbon were used as the precursor gas to grow DLC films, keeping constant the other process parameters. The substrates used were p-type (100) silicon wafers. The films were characterized by Raman spectroscopy, nanoindentation, atomic force microscopy (AFM) and by a profilometer. In order to grow DLC films with special properties that could make this material an alternative candidate for applications in micro-electromechanical systems (MEMS) production, a comparative analysis focused on the influence of the hydrocarbon precursor gas mixture on the mechanical and chemical properties of the DLC films is reported.

6. M.Ueda, K.G. Kostov, A.F. Beloto, N.F. Leite, and K.G. Grigorov,” Surface Modification of polyethylene terephthalate (PET) by Plasma Immersion Implantation” – VII<sup>th</sup> International Workshop on Plasma-Based ion Implantation, Sept. 17-19, 2003, San Antonio, Texas.

**Abstract:** Plasma immersion ion implantation (PIII) of nitrogen has been successfully employed to form an amorphous carbon layer on the surface of 0.25-mm-thick polyethylene terephthalate (PET) sheet used for manufacturing plastic bottles. A DC glow discharge source with controlled floating plasma potential was used to create nitrogen plasma in a 100-l PIII system. The polymer specimens were pulsed (through a metallic grid or sample holder) at repetition rate of 300 Hz with high negative voltage pulse of 10 kV magnitude and 80  $\mu\text{s}$  duration. Formation of carbon film on the PET surface as a result of nitrogen ion implantation was investigated using Raman spectroscopy, optical and atomic force microscopy (AFM). The obtained Raman spectra reveal that the amorphous carbon layer has diamond-like characteristics. AFM micrographs demonstrate that after PIII treatment, the PET surface became much smoother and no cracks were found on it.

7. I.C.Oliveira, K.G.Grigorov, H.S.Maciel, M.Massi, C.Otani, “*High textured AlN thin films grown by RF magnetron sputtering; Composition, structure, morphology and hardness*”, *Vacuum* **75** (2004) 331-338.

**Abstract:** High quality thin aluminum nitride (AlN) films have been deposited onto a silicon (1 0 0) substrate by radio frequency magnetron sputtering of a pure Al target using different gas (Ar, N<sub>2</sub>) mixtures. The depositions were carried out at substrate temperatures varying from room temperature (plasma heating) up to 400\_C. The crystalline structures were investigated by X-ray diffractometry (XRD) revealing a pronounced texture of the deposited films. Some of the compounds investigated were deposited onto a thin buffer layer of pure Al. The film surface morphology was investigated by Atom Force Microscopy (AFM) (SPM-9500J3 from Shimadzu Co), and was found to depend distinctively upon the different deposition conditions. Generally, two kinds of structures were found—a columnar one, which was densely packed or organized in planar parallel sheets, and a flat structure, (typical for mono-crystals), with rms roughness below 0.2 nm. In this paper, the influence of argon added to the sputtering gas environment on the film properties is investigated and discussed. The depth elemental distributions were calculated using 2.4MeV <sup>4</sup>He<sup>+</sup> Rutherford Backscattering Spectrometry (RBS). Finally, the mechanical characteristics were described using hardness tests.

8. Ch. Dikov, M.Marinov, H.Maciel, K.Grigorov, I. Nedkov, G.Beshkov, “*Properties of Cr and Mo Thin Films Deposited by RF sputtering system*” *Journal of Optoelectronics and Advanced Materials* Vol. 7, No. 1, February 2005, p. 385 – 387.

**Abstract:** This report summarizes our recent efforts to produce a good quality Cr and Mo thin films for use in Cu(InGa)Se<sub>2</sub> (CIGS) based solar cells. The surface morphology and the resistivity of Cr and Mo films with various thicknesses ranging from 280 to 750 nm were investigated. The films were deposited in a Tokyda-CPF-4EF RF sputtering system, at powers ranging from 100 to 250 W in a 1 Pa argon atmosphere. The substrate temperature was about 200°C. The deposition rate did not exceed 900 nm/h. The morphology of the films was studied by SEM, and the resistivity was measured by a Four Point Probe method. A correlation was established between the surface morphology (grain size), the resistivity, and the deposition parameters of the Cr and Mo-based layers.

9. K.G.Grigorov, I.Nedkov, G.Beshkov, Ch.Angelov, H.S.Maciel, W.Matz, R.Groetzchel, “*AlN films obtained by broad energy nitrogen ion implantation and Rapid Thermal Annealing Process*” *Journal of Optoelectronics and Advanced Materials* Vol. 7, No. 1, February 2005, p. 381 – 384.

**Abstract:** The paper describes structural, morphological and electrical investigations of thin AlN films. The films were obtained by broad energy range ion bombardment (BERIB) of aluminium, with doses ranging from  $1.5 \times 10^{17} \text{ cm}^{-2}$  to  $6 \times 10^{17} \text{ cm}^{-2}$ . This technique, to our knowledge, has not been described previously in the literature. The ion implantation was carried out with two species - nitrogen atoms with energies from 50, 30, and 20 keV and nitrogen ions with energies of 50 and 30 keV. These energy values were chosen in order to ensure a continuous and wide nitride layer, at least of 150 nm thick.

11. Beshkova M., Grigorov K.G., Zakhariev Z., Abrashev M., Massi M., and Yakimova R., "Sublimation Epitaxy of AlN layers grown by different conditions on 4H-SiC substrates" *Journal of Optoelectronics and Advanced Materials* Vol. 9, No. 2, February 2007, p. 213-216

**Abstract:** Epitaxial layers of aluminium nitride were grown at temperature 2100 °C on 10x10 mm<sup>2</sup> 4H-SiC substrates via a sublimation-recondensation method in an RF heated graphite furnace. The source material was polycrystalline sintered AlN. Growths of AlN layers in vacuum and pure nitrogen at 20 mbar were compared. MA maximum growth rate of 70 μm/h was achieved in a pure N<sub>2</sub> atmosphere. The surface morphology reveals the hexagonal symmetry of the seeds, suggesting an epitaxial growth. This was confirmed by High-Resolution X-Ray Diffraction. The spectra showed a strong and well defined (0002) reflection positioned at 36.04° in a symmetric θ-2θ scan for both samples. Micro-Raman spectroscopy revealed that the films had a wurtzite structure. Rutherford Backscattering Spectrometry indicated the quality with a relative  $\chi_{min}$  parameter 0.68.

12. K.Grigorov, "YBCO PHASE TRANSFORMATIONS STUDIED BY REAL TIME SYNCHROTRON RADIATION", *Revista Brasileira de Aplicações de Vácuo*, v. 25, n. 1, 31-35, 2006.

**Abstract:** The goal of this paper is to investigate the phase transformations of thin multi-layer structures from High Temperature Superconductor -  $YBaCuO_{7-8}$  (YBCO) and manganate -  $La_{0.7}Sr_{0.3}MnO_3$  (LSMO, both deposited on different substrates by means of real-time synchrotron X-ray scattering. The phase formations and phase interaction process were in situ examined in oxygen atmosphere and high temperature. The latter was only possible using SR at Rossendorf Beam Line (ROBL), because the process demands short measuring times in order to follow the process adequately. The temperature ranges of the superconducting phases were also described analyzing the lattice parameter and the peak evolutions. The formation of new un-expected phases was registered. We established the general temperature range of the superconducting YBCO phase formation. To attain this purpose a special vacuum chamber was constructed to fit the goniometer and to work in oxygen atmosphere at elevated temperatures.

13. R.S. Pessoa, G. Murakami, G. Petraconi, H.S. Maciel, I.C. Oliveira, and K.G. Grigorov, "Hollow cathode magnetron deposition of AlN thin films: Crystalline structure and morphology" *Brazilian Journal of Physics* 36(2A) 332, 2006.

**Abstract:** A new dc hollow cathode plasma source has been assembled with a conventional planar magnetron cathode used together with another plane cathode plate to form a hollow cathode cavity. The system comprises two cathode plates of aluminium separated by a distance d, one of them acting as target of the magnetron cathode, the other being an ordinary plate. The discharge anode is a metallic flange of the vacuum chamber. This leads to enhanced ionization in the cathode cavity region and enables the discharge to operate at significantly lower pressures than for a typical planar magnetron configuration. As a consequence, sputtered atoms can reach a substrate with minimum energy loss due to collisions with filling gas atoms. The discharge gas was a mixture of argon and nitrogen. AlN thin films were grown on silicon substrates, at ambient temperature, and characterized with respect to the structure and morphology by XRD and AFM analyses respectively. The structure and roughness of the AlN films were studied as a function of the deposition parameters.

14. J.S. Marcuzzo, W.I. Urruchi, M. Massi, K. Grigorov, H. Maciel, "Use of Oxygen discharge at near atmospheric pressure for DLC films etching", *ECS Transactions, Volume 4, Issue 1, 2006, Electrochemical Society* pp. 545-552

**Abstract:** Diamond-Like Carbon (DLC) films are promising materials for micro and nano-electronic industries, by their particular physical-chemical properties. For these applications, DLC films are usually etched by using plasma reactors that operate at low gas pressure thus requiring sophisticated vacuum and gas admission systems. In this work a much simple and inexpensive plasma etching system was used which is based on a dielectric barrier discharge (DBD), operating with oxygen at near atmospheric pressure. The DBD was integrated to a working chamber where a substrate holder was placed to intercept the plasma flow at a distance from the discharge outlet. The performance of the etch process in this system was evaluated by etching DLC films under various operating conditions: pressures in the range (55.0-75.0) kPa, time of process varying from 1min to 20min and electrode-substrate distance (5 and 10 mm). The main characterization techniques to analyze the etched films were atomic force microscopy (AFM), Raman spectroscopy and profilometry. The results show that etching rates up to 7nm/min can be attained with power as low as 2.3W for a 2.0cm<sup>2</sup>exposed area. Overall, the etching process in this high pressure oxygen plasma medium differs substantially from the case of low pressure etching. It causes low damage to the substrate and promotes more homogeneous etching.

15. Grigorov K., Massi M., Maciel H.S., Freita F. M., Toku H., and Pessoa R.S, "Etching of DLC films exposed to a plasma jet" *Journal of Optoelectronics and Advanced Materials Vol. 9, No. 2, February 2007, p. 382-385*

**Abstract:** In this work, an argon plasma jet was used to etch diamond-like carbon (DLC) thin films, which were grown on silicon (100) substrates by magnetron sputtering. The etching rates of the DLC material were investigated with respect to the ion energy, ion density, magnetic field intensity and plasma power for both perpendicular and inclined incidence of the plasma jet on the substrate. It was observed that the DLC etching rates (around 2-20 nm/min) increased up to 7-fold when the magnetic field in the jet plasma region increased from zero to 6 mT. In addition, at a fixed cathode potential, a reduction in the etching rates was observed for angles of incidence lower than 90°. In order to explore in detail the surface changes due to the etching process, on a nanometric scale, the DLC films were analyzed by atomic force microscopy. The results indicated that by using this etching technique it was possible to reduce the formation of needle-like structures on the etched DLC surface.

16. Pessoa R. S., Murakami G., Massi M., Maciel H.S., Grigorov K.G., da Silva Sobrinho A.S., Petraconi G., Marcuzzo J.S., "Off-axis growth of AlN thin films, by hollow cathode magnetron sputtering under various nitrogen concentrations", *Diamond and Related Materials, V.16, Issue 4-7 (2007) pp. 1433-1436. DOI:10.1016/j.diamond.2006.11.030*

**Abstract:** Amorphous and crystalline AlN thin films were deposited on Si (100) substrates by off-axis hollow cathode magnetron technique. The evolution of the crystalline orientation and the morphology of AlN thin films have been investigated depending on the nitrogen concentration. It has been demonstrated by using a combination of mass spectrometry, X-ray diffraction and atomic force microscopy techniques, that the film crystallinity and surface roughness are related with the nitrogen concentration. The results show that the monitoring of Al<sup>+</sup> and AlN<sup>+</sup> species by mass spectrometry proved to be an important new method to prescribe the plasma conditions for growing amorphous or crystalline films.

17. T. Koutzarova, S. Kolev, K. Grigorov, Ch. Ghelev, I. Nedkov, M. Ausloos, R. Cloots, T. Midlarz, A. Zalesky, "Nanosized Barium Hexaferrite Powders Obtained By A Single Microemulsion Technique" *Solid State Phenomena Vol. 140 (2008) pp 55-60 (2008) Trans Tech Publications, Switzerland*

**Abstract:** Barium hexaferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) powders of particle size of 130 and 180 nm were synthesized by a single microemulsion technique. The influence of the concentration of  $\text{Ba}^{2+}$  and  $\text{Fe}^{3+}$  metallic ions in the aqueous phase in the microemulsion system on the particle size distribution, crystallinity and magnetic properties of  $\text{BaFe}_{12}\text{O}_{19}$  was studied. The coercive force and saturation magnetization of the sample obtained at a lower concentration of metallic cations in the aqueous phase were higher than those of the sample obtained at higher concentration.

18. T. Koutzarova, S. Kolev, K. Grigorov, Ch. Ghelev, A. Zalesky, R.E. Vandenberghe, M. Auslos, C. Henrist, R. Cloots, I. Nedkov, "Structural and magnetic properties of nanosized barium hexaferrite powders obtained by microemulsion technique" *Solid State Phenomena, Vol. 159, 2010, pp. 57-62*

**Abstract:** Thin hexagonal barium hexaferrite particles synthesized using the microemulsion technique were studied. A water-in-oil reverse microemulsion system with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant, n-butanol as a co-surfactant, n-hexanol as a continuous oil phase, and an aqueous phase were used. The microstructural and magnetic properties were investigated. The particles obtained were mono-domain with average particle size 280 nm. The magnetic properties of the powder were investigated at 4.2 K and at room temperature. The saturation magnetization was 48.86 emu/g and the coercivity,  $2.4 \times 10^5$  A/m at room temperature. The anisotropy field  $H_a$  and magneto-crystalline anisotropy  $K_1$  were  $1.4 \times 10^6$  A/m and  $2.37 \times 10^5$  J/m<sup>3</sup>, respectively.

19. Koutzarova T., Nedkov I., Grigorov K., Kolev S., Vandenberghe R. E., Mathieu J.-Ph., Ausloos M., Ghelev Ch., Palewski T., Gajda D., "Structural and magnetic properties of nanosized barium hexaferrite powders obtained by microemulsion techniques", *Nanoscience& Nanotechnology - Proc. of 8th Workshop on Nanostructured Materials Application and Innovation Transfer*, ed. by Balabanova E., Dragieva I., Heron Press Ltd. 56 - 58, (2007)

**Abstract:** In this paper we study the possibility to synthesize thin barium hexaferrite particles by microemulsion technique. We used a water-in-oil reverse microemulsion system with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant, n-butanol as a co-surfactant, n-hexanol as a continuous oil phase, and an aqueous phase. The microstructural and magnetic properties were investigated. The obtained particles were mono-domain with an average particle size 280 nm. The magnetic properties of the powder were studied at 4.2 K and at room temperature. The saturation magnetization was 48.86 emu/g and the coercivity - 3 kOe at room temperature.

20. Freitas F.M., Maciel H.S., Petracono G.F., Grigorov K., Massi M., *Plasma etching of DLC Films using a constricted Hollow Cathode, Revista Brasileira de Vacuo, V. 26, No 3. 131-133, (2007)*

**Abstract:** Thin films are etched in a recently developed modality of high vacuum reactor. Diamond-like Carbon films manufactured by sputtering technique are used to the plasma etch studies. A constricted hollow cathode (CHC) is used as Argon plasma source. To reach etching characteristics adequate to the

microelectronic processes, extensive experiments are carried out to estimate the influence of several control parameters. Bias voltage technique is employed for energetic ion extraction from the produced plasma jet. Helmholtz coil applies an axial magnetic field for improved plasma confinement. The effect of varying bias voltage, magnetic field intensity and plasma power on etch rate has been studied. The bias voltage determines the sputtering yield through the acceleration of Ar ions extracted from the CHC originated plasma jet. The applied magnetic field drives the ion flux to the substrate. Ion flux adjust is also attained by plasma power selection. The results show that the processes in high vacuum with the presence of moderate magnetic fields offer some potential advantages of this technique in comparison to the standard plasma etching processes.

21. Koutzarova T., Kolev S., Ghelev Ch., Grigorov K., Nedkov I., “*Structural and magnetic properties and preparation techniques of nanosized M-type hexaferrite powders*”, *Advances in Nanoscale Magnetism*, Vol. 22, pp. 183-203, Springer Berlin Heidelberg pp. 183-203, 5, (2008)

**Summary:** In recent years, the scientific efforts of a large number of research teams have been concentrating on developing, exploring and applying nanosized magnetic ferroxides. In this review, we consider the fundamental structural and magnetic characteristics of nanosized particles of barium hexaferrite. We discuss in some detail the most common techniques for preparation of nanosized ferroxide powders. Finally, we present original results on applying a promising chemical technique, namely, the single microemulsion technique, for the synthesis of barium hexaferrite powders consisting of homogeneous in shape and size particles.

22. Staneva A., Stoyanova-Ivanova, A., Terzieva, S., Shoumarova, J., Grigorov, K., Zaleski, A., Mikli, V., Angelov, Ch., Dimitriev, Y., BSCCO ceramics doped with ferromagnetic phases, *Journal of Optoelectronics and Advanced Materials*, 11, Issue 10 (2009) 1541-1544

**Abstract:** Bulk superconducting BSCCO ceramics involving a manganite phase have been obtained by two different methods: solid state synthesis and a low temperature sol-gel method. The microstructure of these materials was studied by scanning electron microscopy (SEM), X-ray diffraction and using the method of energy dispersive spectroscopy (EDX). The results suggest that the composites reveal superconductivity (at 86.6K). The obtained samples have dense structures, which preserve the La-manganite phase as fine grains on the boundary with Bi phases. This composite is a potential candidate as a multifunctional material for applications in microelectronics.

23. M.S. Oliveira Junior, S.A.C. Mello, K. Grigorov, M. Massi, A.S. da Silva Sobrinho, H.S. Maciel, J.C.N. Dutra, “*Surface Modification of EPDM Rubber by Microwave Excited Plasmas*”, *Surface Engineering*, Vol. 26 (2010), No 7, 519-524, ISSN: 02670844

**Abstract:** In the present work, a microwave excited plasma (2.45 GHz, 1 kW) was used to modify the surface characteristics of the ethylene propylene diene monomer rubber. The samples were treated with a mixture of nitrogen, hydrogen and argon plasmas. The operating gas pressure was in the 0.2–1 Torr range, the gas flow rate between 5 and 100 sccm and the treatment time varied from 10 to 600 s. The influence of the plasma treatment on the superficial characteristics of the samples was analyzed by contact angle measurements and atomic force microscopy. The results show that the plasma treatment can promote an

important decrease in the contact angle from  $10^\circ$  for untreated sample to  $34^\circ$  for samples treated in a mixture of  $H_2/N_2/Ar$  for 2 min, which corresponds an increase on the rubber surface adhesion work from 59 to  $133 \text{ mJ m}^{-2}$ .

24. D. A. Duarte, M. Massi, A. S. da Silva Sobrinho, H. S. Maciel, K. Grigorov, L. C. Fontana, "Titanium dioxide thin film deposition by direct current hollow cathode magnetron sputtering", *European Physical Journal, Applied Physics* 49, (2010) 1307-1310, ISSN: 1286-0042

**Abstract:** Cylindrical hollow cathode magnetron sputtering (HCMS) system was used to deposit crystalline titanium dioxide thin films on p-Si (100) substrates. For a fixed pressure of 0.6 Pa total gas flow rate of 20 sccm and power of 55 W, the influence of the oxygen percentage in the Ar+O<sub>2</sub> gas mixture on the structural and surface properties of the films was studied by profilometry, XRD and AFM. The substrates were placed inside the hollow cathode at different positions along its symmetrical axis. Numerical simulations of cathode ion collection probability (CICP) were done in order to compare calculated data with the deposition process characteristics. The results indicate that the deposition rate and the surface roughness gradually decrease with the distance from the bottom of the cathode, due to the decrease of the CICP. The increase of the oxygen percentage in the gas discharge influences directly the deposition rate and decrease the surface roughness. The XRD analyses show that all the films are crystalline with predominant anatase (101) and rutile (110) orientations.

25. B N Sismanoglu, K G Grigorov, R Caetano, M V O Rezende and V W Ribas, *Spectroscopic diagnostics and electric field measurements in the near-cathode region of an atmospheric pressure microplasma jet*, *European Physical Journal D*, (2010) 479-487, ISSN: 1434-6060

**Abstract:** Linear Stark splitting of the  $H_\beta$  Balmer line components and spatially resolved optical emission spectroscopy (OES) measurements were used to estimate the electric field gradient in the cathode sheath region ( $\sim 70 \mu\text{m}$  long) of an atmospheric pressure direct current argon flow-stabilized microplasma jet. Also, plasma parameters in the negative glow region were investigated by both OES and electrical diagnostics. The microplasma jet was operated for current ranging from 10 to 110 mA. OH ( $A \ 2\Sigma^+$ ,  $v = 0 \rightarrow X \ 2\Pi$ ,  $v' = 0$ ) rotational bands at 306.357 nm and also the Ar 603.213 nm line were used to determine the gas temperature, which ranges from 600 to 1000 K. Electron number density, ranging from  $4.1 \times 10^{14}$  to  $8.5 \times 10^{14} \text{ cm}^{-3}$ , was determined through analysis of the  $H_\beta$  line. Electron excitation temperature was also measured from the ratio of two Mo lines (8500–18 000 K) and from Boltzmann-plot of Ar 4p–4s and 5p–4s transitions (11 000–13 500 K).

26. B N Sismanoglu, K G Grigorov, R Caetano, M V O Rezende and Y D Hoyer, *Spectroscopic measurements and electrical diagnostics of microhollow cathode discharges in argon flow at atmospheric pressure*, *European Physical Journal D*, Vol. 60, (2010) 505-516, ISSN: 1434-6060.

**Abstract:** This paper is dedicated to the study of the electrical and optical characteristics of direct current microhollow cathode discharges (MHCD) in argon flow. Experiments have been carried out in order to determine the so-called Paschen's curves in a static open MHCD. Current-voltage characteristics were obtained as a function of the pressure and hole diameter. MHCD enable stable direct current discharge operation, which could be ignited for pressures ranging from 12 to 800 Torr, in a very wide range of current densities and electrodes materials. Optical emission spectroscopy and analysis of the spectral line broadening of plasma line emissions were performed in order to measure parameters such as electron number density ( $2\text{--}4 \times 10^{14} \text{ cm}^{-3}$ ), gas temperature (460–640 K), excitation temperature ( $\sim 7000 \text{ K}$ ) and

electron temperature ( $\sim 8500$  K), for current ranging from 7 to 15 mA. Lower gas temperature was measured compared to the static MHCD ones.

27. B N Sismanoglu, C.L.A. Cunha, M.P. Gomes, R. Caetano, K.G. Grigorov, *Optical and electrical diagnostics of microdischarges at moderate to high pressure in argon*, ***Brazilian Journal of Physics***, Vol. 40, no 4, December, 1-5 (2010) ISSN: 01039733.

**Abstract:** Microdischarges at moderate to high pressure in argon were investigated. A hole opening diameter of 500  $\mu\text{m}$  direct current (dc) microhollow cathode discharges (MHCD) were characterized by electrical measurements and optical emission spectroscopy (OES) for pressures ranging between 90 and 800 Torr and current from 5 to 20 mA. Current-voltage characteristic curves were obtained as a function of the pressure for this hole diameter. MHCD enables stable dc discharges for molybdenum electrodes material at constant Ar + 2% $\text{H}_2$  flow of 0.03 l/min. Optical emission spectroscopy and analysis of the spectral line broadening of plasma line emissions were performed in order to measure gas discharge parameters. Electron number densities were obtained from  $\text{H}_\beta$  Balmer line ( $\sim 10^{14}$   $\text{cm}^{-3}$ ). For the above mentioned discharge conditions, gas temperature was estimated to be 550 – 850 K from OH rotational bands. Excitation temperature was measured based on two lines method (from atomic Mo lines) and from 4p - 4s and 5p – 4s Ar radiative transitions. Hydrogen atom temperature was measured for 800 Torr ( $\sim 12000$  K).

28. K G Grigorov, I C Oliveira, H S Maciel, M Massi, M S Oliveira Jr, J Amorim, C A Cunha, “*Optical and morphological properties of N-doped TiO<sub>2</sub> thin films*”, ***Surface Science*** 605 (2011) 775-782.

**Abstract:** Nitrogen doped titanium dioxide (TiO<sub>2</sub>) thin films were deposited by RF magnetron sputtering onto various substrates. The films were prepared in plasma of argon, oxygen, and nitrogen, with varying the nitrogen content, from 0% up to 70%. The resulting TiO<sub>x</sub>-N<sub>y</sub> films were found to consist of cubic TiN osbornite and tetragonal TiO<sub>2</sub> rutile phases. Using optical spectroscopy with large spectral range from 350 to 1000 nm, the band gap width was determined and a narrowing of the optical gap from 2.76 to 2.32 eV was observed as a function of the N-content. It was found that the optical properties of the TiO<sub>x</sub> N<sub>y</sub> layers are influenced by the surface morphology, roughness, surface energy and phase content. The chemical composition, the crystalline structure, the surface morphology and the surface energy were thoroughly studied by the Rutherford backscattering spectrometry (RBS), grazing-angle XRD, atomic force microscopy (AFM) and contact angle measurements (wettability), respectively.

29. R. K. Yamamoto, R. S. Pessoa, M. Massi, K. Grigorov, M. R. Gongora-Rubio, H. S. Maciel, “*Surface modification of polyethylene by a medium pressure micro-plasma generator*”, ***Surface Engineering***, Vol. 27, Issue 2 (2011) 80-86.

**Abstract:** Polyethylene surface modification studies were performed in a new microplasma source using O<sub>2</sub> and N<sub>2</sub> gases. The degree of modification of polyethylene surface was qualitatively investigated through water contact angle measurements using distilled water. The influence of the plasma discharge parameters, such as gas nature, gas flow, power and exposure time, over the polyethylene contact angle was investigated. The obtained results indicate a decrease of the contact angle from 100° (for untreated sample) to 22.9°, when N<sub>2</sub> plasma was used for 40 s and discharge power >2 W. The surface morphology of the samples was examined by atomic force microscope and a smoothing effect after the plasma treatment was found. These results are very promising because of the experimental set-up which requires

medium vacuum, exhibit low process temperature (50–100°C) leaving the surface intact. Other advantages are the very short processing time (60 s) and applicability to large area substrates.

30. M Beshkova, K Grigorov, I Nedkov, M Massi, B Sismanoglu, H Maciel, and N B Velchev, “Properties of thin silicon carbide films prepared by rapid thermal annealing”, *Journal of Physics: Conference Series* **356** (2012) 012039 doi:10.1088/1742-6596/356/1/012039

**Abstract:** We report experimental results related to the structural and electrical properties of thin SiC films. Thin carbon films with thicknesses 50 Å and 300 Å were deposited by R.F. sputtering and processed by rapid thermal annealing (RTA) for 3 min at temperatures of 800 oC and 1400 oC in a vacuum chamber at  $2 \times 10^{-5}$  Torr. The thin films properties were studied by Raman spectroscopy and electrical cross-conductance.

31. Y. D. Hoyer, B. N. Sismanoglu, and K.G. Grigorov, “Measurements of spatially resolved electron number densities and modes temperatures using optical spectroscopy of atmospheric pressure microplasma jet”, *European Physical Journal D*, (2012) 66: 171, DOI:10.1140/epjd/e2012-20727-y

**Abstract:** The electrical gas discharge parameters of direct-current non-thermal microplasma jet in Ar-2% H<sub>2</sub> flow at open atmospheric air was investigated by using spatially resolved optical emission spectroscopy (OES). The jet was confined from microhollow of tungsten-carbide (~500 μm inner diameter) to a molybdenum foil. Despite its small volume, the atmospheric pressure microplasma jet provides a range of power densities, from low to ~1012 W m<sup>-3</sup> generated either in rare gases or in molecular gases. A high resolution spectrometer (Jobin-Yvon, Czerny-Turner model THR1000, resolution of 0.001 nm, with focal length of 1.0 m and numerical aperture of 0.13 – f/7.5) was used to allow registration of OH (A<sup>2</sup>Σ<sup>+</sup>, ν = 0 → X<sup>2</sup>Π, ν' = 0) rotational bands at 306.357 nm, Ar I 603.213 nm line and N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub>, ν = 0 → B<sup>3</sup>Π<sub>g</sub>, ν' = 0) second positive system with the band head at 337.13 nm in order to estimate the rotational temperature from the cathode sheath of the plasma jet to the anode. For currents ranging from 20 to 100 mA and for a particular excited levels, the excitation temperature was measured in the negative glow region either from a Boltzmann plot of Ar I 4p–4s and 5p–4s transitions of excited argon or using the Mo I (from 440 to 450 nm) two-lines method of excited Mo atoms sputtered from the cathode surface, giving 24 000 K (100 mA at 100 μm) and 7000 K (20 mA at 500 μm from the cathode). From the N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub>, ν = 0 → B<sup>3</sup>Π<sub>g</sub>, ν' = 0) rotational transition the rotational temperature along the positive column was estimated. The vibrational temperature of the bulk plasma (1400 to 4500 K) was estimated for a current varying from 20 to 120 mA using the N<sub>2</sub> second positive system with Δν = -2. Using the broadening of H<sub>β</sub> Balmer line it was possible to estimate the electron number density of the negative glow (1014 to 1015 cm<sup>-3</sup>) as a function of the current.

32. R. Caetano, Y. D. Hoyer, I. M. Barbosa, K. G. Grigorov and B. N. Sismanoglu, “Radial measurements of gas discharge parameters of atmospheric pressure microplasma”, *International Journal of Modern Physics B*, Vol. 27, No.18 (2013) 1350089 (13 pages) DOI: 10.1142/S0217979213500896

**Abstract:** In this work Abel inversion technique was used for radial measurements of the microplasma in Ar-2%H<sub>2</sub> flow at open atmosphere. The gas discharge parameters were investigated using spatially resolved high resolution optical emission spectroscopy (OES) to allow acquisition of OH (A<sup>2</sup>Σ<sup>+</sup>, ν = 0 → X<sup>2</sup>Π, ν' = 0) rotational bands at 306.357 nm, Ar I 603.213 nm line and N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub>, ν = 0 → B<sup>3</sup>Π<sub>g</sub>, ν' = 0) second positive system with the band head at 337.13 nm. The nonthermal plasma was generated between

microhollow anode ( $\sim 500 \mu\text{m}$  inner diameter) and a cathode copper foil, fed by direct current source for a current ranging from 20 mA to 100 mA (Townsend discharge from 20 mA to 30 mA, normal glow discharge from 30 mA to 80 mA at 210 V and abnormal discharge beyond 90 mA). The 1.5 mm length cylindrical-shape plasma has an outspread bright disk (negative glow region) near the cathode surface. Besides the gas temperature, the excitation temperature was measured radially for a current ranging from 20 mA to 100 mA, either from Boltzmann-plot of Ar I 4p – 4s and 5p – 4s transitions of excited argon or from Cu I two lines method of excited cuprum atoms released from the cathode surface. The measurements showed a nearly bell-shaped distribution of these temperatures, peaked at 120  $\mu\text{m}$  from the center with the minimum at the plasma border. The average excitation temperature was about  $\sim 8000 \text{ K}$  (maximum  $\sim 10,000 \text{ K}$ ) and the average rotational temperature was about 650 K (maximum  $\sim 800 \text{ K}$ ) from 20 K to 100 K. For the  $\text{N}^2$  second positive system with  $\Delta v = -2$  it was estimated the vibrational temperature for the bright disk (1500 K to 5000 K).  $\text{H}_\alpha$  line Stark broadening was employed to define the electron number density of the negative glow ( $10^{15} \text{ cm}^{-3}$ ).

33. Libardi, J, Grigorov, K.G., Guerino, M, da Silva Sobrinho, A.S., Maciel, H.S, Massi, M., “High quality  $\text{TiO}_2$  deposited by reactive sputtering. Structural and electrical peculiarities influenced by the specific experimental conditions”, **IEEE - Microelectronic Technology and Devices (SBMicro)**, 2013 Symposium, 2-6 Sept. 2013, 1-4, ISBN: 978-1-4799-0516-4, DOI: 10.1109/SBMicro.2013.6676130

**Abstract:** Titanium dioxide ( $\text{TiO}_2$ ) thin films were deposited on silicon p type (100) substrates by reactive magnetron sputtering technique at different oxygen partial pressures. The film structure was studied by X-Ray Diffraction (XRD), while the film composition was examined by Rutherford Backscattering Spectroscopy (RBS). Finally, Metal-Oxide Semiconductor (MOS) capacitors were manufactured and some important physical constants were analyzed as function of the oxygen content in the films. It was found that the films deposited at lower oxygen partial pressure exhibited better crystalline structure and higher dielectric constant.

34. B. N. Sismanoglu, R. S. Pessoa, R. Caetano, Y.D. Hoyer, H. S. Maciel and K. G. Grigorov, “Argon Properties, Production and recent Applications” Chapter 1, In: Argon: Production, Characterization and Applications, 2013 Nova Science Publishers, Inc. ISBN: 978-1-62618-204-2

**Abstract:** Argon is a noble gas that is present in the Earth's atmosphere at approximately 1% and is produced industrially by the partial distillation of liquid air. It is a by-product of the oxygen and nitrogen production. Argon is the most commonly used gas in research, industry, medicine (dermatology, ophthalmology), analytical chemistry, nanotechnology and plasma technology due to its excellent thermal performance and cost-efficiency in comparison to other noble gases. This chapter presents some characteristics and production methods of argon and, finally, provides various applications in diverse areas of human knowledge. Argon isotopes  $^{40}\text{Ar}/^{39}\text{Ar}$ , applied to geochronology and thermo-chronology to date the age of ancient materials, such as rocks and fossils. Low temperature atmospheric-pressure argon plasmas are relatively new contributions for diagnostics and medical applications, whereas electrical and optical studies of these discharges are in course nowadays.

35. M. Radmilović-Radjenović, B. N. Sismanoglu, B. Radjenović and K. G. Grigorov, “Modeling of the Breakdown Voltages in Argon Discharges with Improved Secondary Electron Emission

**Abstract:** This chapter relates on results obtained by both theoretical and simulation studies based on the breakdown dc voltage, as well as on the microwave discharges in argon atmosphere with and without magnetic field presence. Emphasizes were given on the role of the secondary emission processes on the breakdown voltage. Calculations were performed using a Particle-in-cell/Monte Carlo collisions (PIC/MCC) code with the secondary emission model adjusted to account the energy and angular dependence of the electron yield at large separations, as well as the secondary electron emission enhanced by field emission micrographs. For high frequency discharges, the breakdown voltage - frequency dependence was analyzed and a simple scaling law was suggested. In crossed or parallel electric and magnetic fields, the breakdown voltage was determined taking into account the electron yield variations with magnetic field. The presented results indicate that PIC/MCC code with improved secondary emission model provides a good physical description of the plasma processes for various gap sizes in presence of electric field under the simultaneous action of both electric and magnetic fields. The simulation data obtained are in good agreement with the experimental results. Apart from their theoretical significance, the obtained results could be useful for determining the minimum ignition voltages in microplasma sources, as well as the maximum safe operating voltage and critical dimensions in other micro-devices.

36. J. C. Nascimento, E. C. B. B. Aragão, A. D. Fernandes, F. T. F. Barbosa, L. M. S. Costa, D. C. Sousa, C. Oliveira, G. J. P. Abreu, K. G. Grigorov, P. Getsov, R. S. Pessoa, V. W. Ribas, B. N. Sismanoglu, “Optical Measurements of an Atmospheric Pressure Microplasma Jet Aiming Surface Treatment”, *American Journal of Condensed Matter Physics*, 2014, 4(3A): 8-18, DOI: 10.5923/s.ajcmp.201401.02

**Abstract:** In this work stable non-thermal ac high voltage atmospheric pressure microplasma jet (APMJ) device was used for optical and electrical characterizations. It enables the generation of low power (~5W) microplasma jet at frequency of 60Hz. The jet has a visible radial diameter of approximately 1.5 mm. Optical emission spectroscopy was used as a diagnostic tool to determine the gas discharge parameters as the modes temperature. The rotational temperature of OH radicals at the exit nozzle varies from 325 to 525K for different gases where the electrical input power ranged from 3 to 10W. Both the electronic (0.5 – 0.7eV) and vibrational temperatures (0.35 – 0.58eV) were estimated at the same power conditions for Ar, He, N<sub>2</sub>, air and O<sub>2</sub> + 1%Ar flow rates. The highly reactive species as OH, O, N<sup>2+</sup> and the energetic photons produced between the electrodes extent along the plasma plume, both in radial and axial direction from the exit of the APMJ.

37. C. Oliveira, F. M. Freitas, G. J. P. Abreu, M. P. Gomes, K. G. Grigorov, P. Getsov, I. M. Martin, R. S. Pessoa, L. V. Santos, V. W. Ribas, B. N. Sismanoglu, “Optical measurements of Atmospheric Pressure Direct Current He/H<sub>2</sub> Microplasma in Open Air for Surface Modification”, *American Journal of Condensed Matter Physics*, 2014, 4(3A): 19-27, DOI: 10.5923/s.ajcmp.201401.03

**Abstract:** Gas discharge parameters of a direct current Ar+2%H<sub>2</sub> non-thermal microplasma operated at atmospheric pressure were measured in this work. The microplasma was investigated in the normal and abnormal glow regimes, for current ranging from 10 to 130 mA, at ~ 160 - 250 V of applied voltage for a

cathode formed with Cu+Mo+Fe foils, covered with mica at front face Cu foil. The microplasma goes through an opening hole traversing the dielectric and metal foils and emerging on open air. Both OH ( $A^2\Sigma^+, v = 0 \rightarrow X^2\Pi, v' = 0$ ) and  $N_2 (C^3\Pi_u, v = 0 \rightarrow B^3\Pi_g, v' = 2)$  bands were used to estimate the gas temperature, which ranges from 450 to 800 K. The electron number densities, ranging from  $3.0 \times 10^{14}$  to  $8.0 \times 10^{14} \text{ cm}^{-3}$ , were determined by the  $H_\beta$  line. Excitation temperatures were measured from three methods: from two Cu I and Mo I spectral lines ratio ( $T_{exc} = 2\ 700$  K) and from Boltzmann-plot of both Fe I and He I transitions ( $T_{exc} = 3\ 000$  K). The vibrational temperature was carried out from the second positive system  $N_2 (C^3\Pi_u \rightarrow B^3\Pi_g)$  for  $\Delta v = -2$  and it was in the range 2500 - 3000 K for a current varying from 20 to 100 mA.

38. C. Oliveira, J. C. Nascimento, I.M. Martin, K. G. Grigorov, G. J. P. Abreu, V. W. Ribas, B. N. Sismanoglu, “40 Torr Glow Discharge Used for Polyethylene Treatment”, *American Journal of Condensed Matter Physics*, 2014, 4(3A): 28-31, DOI: 10.5923/s.ajcmp.201401.04

**Abstract:** Spectral and electrical characterizations were carried out on low current (2-8 mA), 40 Torr microplasma device aimed to polyethylene surface modifications, such as wettability (work of adhesion). A mixture of argon and oxygen (2%) was used as working gas and as far as the oxygen is ionized between the electrodes polarize the treated surface resulting in its increased surface energy. The argon has an important role too, as well as it is carrying gas with higher atomic weight providing better efficacy of the process. By conducting optical measurements the plasma parameters was estimated. The average gas temperature was about 350 K for current ranging from 1 to 8 mA at the cathode nozzle exit and was 300 K at 2 mm from the cathode borehole. From the Balmer  $H_\beta$  spectral line it was estimated the electron number density  $n_e = (1.2 \pm 0.2) \times 10^{19} \text{ m}^{-3}$ . The electron excitation temperature was found to be  $T_{exc} = (0.65 \pm 0.05)$  eV. To increase the wettability of the HDPE surface, the best experimental parameters to obtain low contact angle are as follows: flow of 100 ml/min, peak current of 5 mA and operation of 250 s.

39. R. Caetano, Y. D. Hoyer, C. Oliveira, M. S. D. Silva, J. C. Nascimento, G. J. P. Abreu, I.M. Martin, K. G. Grigorov, V. W. Ribas, R. S. Pessoa, B. N. Sismanoglu, “Study of Microhollow Cathode Glow Discharge to Improve the Wettability on Surface of Polypropylene Film”, *American Journal of Condensed Matter Physics*, 2014, 4(3A): 32-39, DOI: 10.5923/s.ajcmp.201401.05

**Abstract:** The ion density distribution has been made and the ionization rate profile has been studied at moderate to atmospheric pressure inside the cavity of microhollow cathode glow discharge to better understand the microplasma behavior, aiming thin film deposition. This methodology sounds as a quite straightforward approach for much investigated, but not well understood, glow discharge at atmospheric pressure. An analytical solution for the continuity equation was proposed, which permits to obtain the ion density distribution and ionization rate profile inside the microplasma. The radial ionization rate has a maximum at the edge of the negative glow where the density of high-energy electrons is higher increasing the number of ionization collisions. The solution of continuity equation shows that microhollow cathode glow discharge has elevated ion density as would be for high-pressure discharges. The results were compared with spectroscopic measurements employing argon and Balmer lines. This microplasma was used as glow plasma based aiming the improvement of the wettability on polypropylene film.

40. J. Libardi, K. G. Grigorov, R. S. Moraes, M. Guerino, A. S. da Silva Sobrinho, M. Massi, “Electrical Conduction Mechanisms in Metal-Insulator\_Metal (MIM) Structure with  $TiO_xN_y$  Thin Films Deposited with Different O/N Ratios” *Journal of ELECTRONIC MATERIALS*, Springer

**Abstract:** In this work, the current–voltage characteristics of titanium oxynitride thin films were measured and the charge carrier transport mechanisms established as a function of film composition. The films were deposited by magnetron sputtering, where the oxygen/nitrogen ratio was varied via a pulsing technique to enable the achievement of desired concentrations. Thus, the obtained films showed metallic titanium nitride (TiN) or semiconductor titanium dioxide (TiO<sub>2</sub>) character and were used to fabricate metal–insulator– metal structures. An ohmic conduction mechanism was identified in the films with higher nitrogen incorporation or presenting TiN-rich phase. Decrease in the nitrogen content resulted in films with TiO<sub>2</sub>-rich phase. In this case, Poole–Frenkel and space-charge-limited current conduction mechanisms were observed. The dielectric constants were calculated from the high-frequency capacitance–voltage dependences, with a reduction from 10 to 3 being observed due to the stoichiometric changes and probable incorporation of defects into the film structure. Finally, the film composition and structural characteristics of the films were revealed by Rutherford backscattering and x-ray diffraction techniques, respectively.

41. W. Chiappim, G. E. Testoni, J. S. B. de Lima, H. S. Medeiros, Rodrigo Sávio Pessoa, K. G. Grigorov, L. Vieira, H. S. Maciel, “Effect of Process Temperature and Reaction Cycle Number on Atomic Layer Deposition of TiO<sub>2</sub> Thin Films Using TiCl<sub>4</sub> and H<sub>2</sub>O Precursors: Correlation Between Material Properties and Process Environment” **Brazilian Journal of Physics, Condensed Matter**, V.45, No. 6, 2015, ISSN 0103-9733, DOI 10.1007/s13538-015-0383-2

**Abstract:** The effect of process temperature and reaction cycle number on atomic layer-deposited TiO<sub>2</sub> thin films onto Si(100) using TiCl<sub>4</sub> and H<sub>2</sub>O precursors was investigated in order to discuss the correlation between the growth per cycle (GPC), film structure (crystallinity), and surface roughness as well as the dependence of some of these properties with gas phase environment such as HCl by-product. In this work, these correlations were studied for two conditions: (i) process temperatures in the range of 100–500 °C during 1000 reaction cycles and (ii) number of cycles in the range of 100–2000 for a fixed temperature of 250°C. To investigate the material properties, Rutherford backscattering spectrometry (RBS), grazing incidence X-ray diffraction (GIXRD), and atomic force microscopy (AFM) techniques were used. Mass spectrometry technique was used to investigate the time evolution of gas phase species HCl and H<sub>2</sub>O during ALD process. Results indicate that the GPC does not correlate well with film crystallinity and surface roughness for the evaluated process parameters. Basically, the film crystallinity relies solely on grain growth kinetics of the material. This occurs due to higher HCl by-product content during each purge step. Furthermore, for films deposited at variable cycle number, the evolution of film thickness and elemental composition is altered from an initial amorphous structure to a near stoichiometric TiO<sub>2-x</sub> and, subsequently, becomes fully stoichiometric TiO<sub>2</sub> at 400 cycles or above. At this cycle value, the GIXRD spectrum indicates the formation of (101) anatase orientation.

42. J. Libardi, K. G. Grigorov, M. Massi, A. S. da Silva Sobrinho, R. S. Pessoa, B. Sismanoglu, “Diffusion of Silicon in Titanium Dioxide Thin Films with different degree of crystallinity: Efficiency of TiO<sub>2</sub> and TiN barrier layers”, **Vacuum**, December 2015, (under review)

**Abstract:** Two kinds of reactively sputtered titanium dioxide films with columnar and fine-grained structures were investigated as diffusion barriers, preventing the silicon diffusion. The only differences in

the deposition conditions were the oxygen percentage concentration (OC) in the discharge, kept for 10% and 30 % of the total working pressure. The resulting films were found to have different thicknesses being 800 and 240 nm for 10% and 30% OC, respectively. The films were studied by X-Ray diffraction spectrometry (XRD) and their composition by Rutherford Backscattering Spectrometry (RBS). In order to describe the diffusion processes, the two batches were annealed up to temperature of 800°C. The diffusivity from 300° to 800°C is  $D(m^2/s) = 2.43 \cdot 10^{-18} \exp[-(15 \text{ kJ/mol})/(RT)]$  and  $D(m^2/s) = 2.36 \cdot 10^{-18} \exp[-(18.4 \text{ kJ/mol})/(RT)]$  for (10% OC) and TiO<sub>2</sub> (30% OC), respectively. The physical meaning of the derived diffusion parameters are discussed in view of the crystalline peculiarities of the obtained films. Arrhenius plots show clearly that higher activation energy is characteristics for films with better-packed crystallites. These results are compared with known diffusion barrier layer such as TiN.