

# New Vapor Deposited Dielectric Polymer Thin Films for Electronic Applications

Stefan Schröder<sup>1</sup>, Thomas Strunskus<sup>1</sup>, Nicolai Ababii<sup>2,3</sup>, Oleg Lupan<sup>2,3</sup>, Nicolae Magariu<sup>2,3</sup>, Franz Faupel<sup>1</sup>

<sup>1</sup> Chair for Multicomponent Materials, Institute for Materials Science, Kiel University, Kaiserstr. 2, D-24143, Kiel, Germany, [ssch@tf.uni-kiel.de](mailto:ssch@tf.uni-kiel.de), [ts@tf.uni-kiel.de](mailto:ts@tf.uni-kiel.de), [ff@tf.uni-kiel.de](mailto:ff@tf.uni-kiel.de)

<sup>2</sup> Center for Nanotechnology and Nanosensors, Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova, [nicolai.ababii@mib.utm.md](mailto:nicolai.ababii@mib.utm.md), [oleg.lupan@mib.utm.md](mailto:oleg.lupan@mib.utm.md)

<sup>3</sup> Department of Microelectronics and Biomedical Engineering Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova, [nicolai.ababii@mib.utm.md](mailto:nicolai.ababii@mib.utm.md), [oleg.lupan@mib.utm.md](mailto:oleg.lupan@mib.utm.md)

**Abstract**—Dielectric materials are of great interest in a vast amount of applications ranging from cable insulation to advanced electronic devices. The emerging trend of device miniaturization is creating an increased demand for dielectric thin films that can be produced precisely on the nanometer scale. In addition, special mechanical properties are often required, for example in the field of flexible organic electronics. Polymers are first-choice materials for this purpose. However, it is extremely difficult to produce precise nanoscale thin films, which have a low defect density and are free of e.g. residual solvent, by wet chemistry approaches. Initiated chemical vapor deposition (iCVD) is a solvent-free polymer thin film deposition process which can be used to produce high quality dielectric thin films with nanoscale control and circumvents thus these problems. This work demonstrates the versatility of the iCVD process in the field of electrical applications by some new application examples of iCVD coatings.

**Keywords**—Polymers, Initiated Chemical Vapor Deposition, Electronic Materials, Dielectrics, Electrets, Gas Sensors

## I. INTRODUCTION

The current advent of polymer thin films enabled by the combination of chemical vapor deposition (CVD) with organic chemistry provides a variety of new pathways in the field of organic electronics and electronic applications. In particular, oxidative chemical vapor deposition (oCVD) and initiated chemical vapor deposition (iCVD) variants developed by Gleason et al. facilitate the precise deposition of new electronic materials from a few nanometers to several micrometers in film thickness. [1] While in oCVD a step growth reaction allows the preparation of conjugated polymers such as PEDOT or

PANI [2], iCVD usually results in insulating films due to the underlying free radical polymerization. In the latter, the polymer backbone is sp<sup>3</sup>-hybridized and the polymer films can be used as dielectrics. Due to the solvent-free nature of iCVD, the dielectric layers are of very high quality and have no defects that accelerate e.g. dielectric breakdown [3]. Thanks to the CVD-typical growth character, the iCVD process can easily be scaled up and integrated into modern microelectronic process lines. A schematic illustration of the iCVD process is shown in Fig. 1a. The respective monomer (M) and initiator (I) are introduced to the reactor. The reactor is equipped with a heatable filament array, located above a sample stage, which is cooled to room temperature. The monomer molecules adsorb at the substrate stage and once the filaments are heated the initiator molecules are decomposed into free radicals (R). These radicals meet e.g. a vinyl groups of the adsorbed monomer molecules. They start a free radical polymerization, which follows similar kinetics like the well-known kinetics for wet chemistry free radical polymerization [4] in order to produce high quality polymer thin films at the substrate surface. In this work, some new application examples of different tailored dielectric iCVD films are shown to demonstrate the versatility of the process in the field of electrical applications.

## II. RESULTS AND DISCUSSION

The application of iCVD thin films as dielectric film is reported by many authors. Especially organocyclosiloxanes like PV3D3 and PV4D4 and fluropolymers have demonstrated excellent performance [5][6][7]. The chemical structure of possible monomers and initiators are presented in Fig. 1b. One argument for

<https://doi.org/10.52326/ic-ecco.2021/EL.02>

using iCVD is the high film quality, because no organic solvent is used. Residual solvent and defects can cause

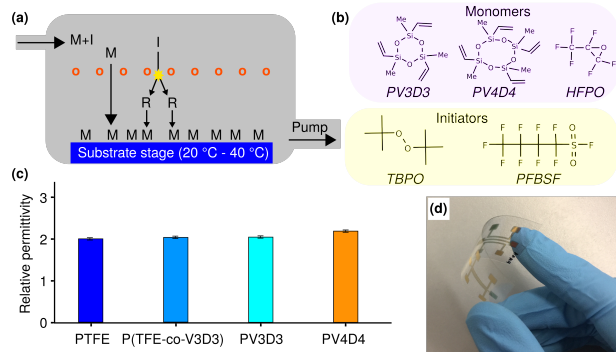


Figure 1. (a) Schematic illustration of the iCVD process. Monomer (M) vapor and Initiator (I) vapor are introduced to a hot wire CVD (HWCVD) reactor. Thermally decomposed I results in free radicals (R), which initiate a free radical polymerization with adsorbed M. (b) Possible monomers and initiators for dielectric thin films. (c) Measurement of relative permittivity for different iCVD thin films. (d) Photograph of flexible iCVD thin film on electronic device.

e.g. conductive paths and lower the dielectric breakdown strength of the material. For dielectric iCVD films the breakdown strength is extremely high, due to a low defect density and high film quality without residual solvent molecules [3]. Fig. 1c shows the relative permittivity of different dielectric thin films grown via iCVD. By using different monomers and initiators or by combining different comonomers the dielectric properties of the film can be individually tuned. The more the chemical composition changes to an organosilicon character the more the dielectric constant increases, as seen from the measurements of PTFE, P(TFE-co-V3D3) and PV3D3. By switching from a cyclotrisiloxane (V3D3) monomer to a cyclotetrasiloxane (V4D4) monomer, as well as different initiators (TBPO), the relative permittivity increases further. The polymer films can in this connection also be deposited on flexible substrates, as shown in the photograph in Fig. 1d and are thus also highly attractive for flexible organic electronics. This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations. Since dielectric iCVD films exhibit high breakdown strength and high film quality, we also demonstrated the use of iCVD grown PTFE thin films as electret materials [3]. Electrets are dielectric materials with a quasipermanent surface charge. They are among others applied in portable electret condenser microphones, energy harvesting, air filters or magnetic field sensors [8][9]. Typically charged by corona discharge, contact electrification or electron beams [10], the surplus charge carriers are stored in the material in trap states. These are additional states in the bandgap of the polymer, as illustrated in Fig 2a. PTFE thin films, PV3D3 thin films and PEGDMA thin films have been charged in a corona

discharge under identical conditions and their charge stability is investigated via thermally stimulated discharge measurements. As shown in Fig. 2b, the PV3D3 films (red curve) show a significant lower charge stability, compared to the other polymers.

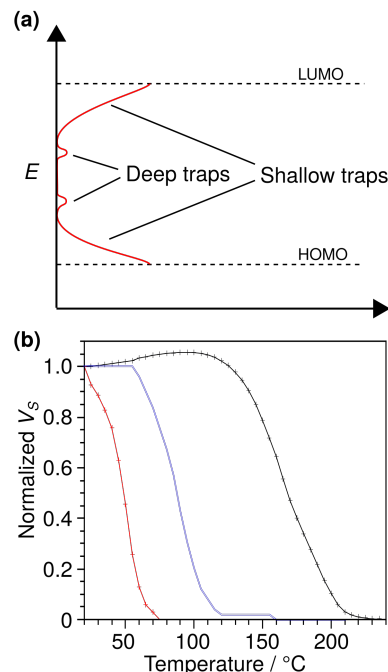


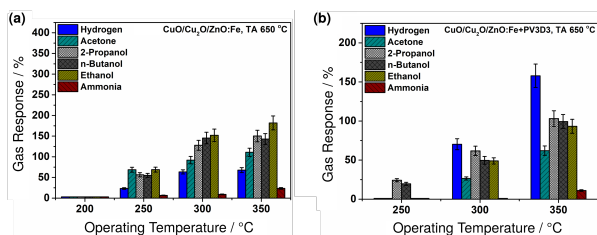
Figure 2. (a) Schematic illustration of deep trap and shallow trap states located in the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). (b) Thermally stimulated discharge measurement for iCVD thin film electrets. Red: PV3D3, Blue: PEGDMA and Black: PTFE.

The surface charge vanishes here nearly directly after the charging. PEGDMA thin films (blue curve) show a better stability than PV3D3, but they are not as stable as PTFE thin films (black curve). This underlines the general observation, that fluoropolymers are one of the best materials for surface charge storage and thus the electret application, because they provide a lot of deep level traps [electretcharging]. Another way to use iCVD for electronic devices such as sensors is, for example, the chemical functionalization of the surface. Here, we have developed a conformal hydrophobic coating for metal-oxide gas sensors, so that the sensors can now be operated in high humidity, which was previously a major problem [11]. The dependence of the gas response (hydrogen, acetone, 2-propanol, n-butanol, ethanol and ammonia) versus operating temperature of the samples is shown in Fig. 3a,b. For comparison Fig. 3a shows the samples without PV3D3 coating and Fig. 3b the samples with PV3D3 coating. For the non-coated samples (Fig. 3a) the highest gas response is to ethanol vapors. After the coating with PV3D3 (Fig. 3b) in addition to the resistance to moisture the sample becomes selective for H<sub>2</sub> gas with the highest response at the operating

<https://doi.org/10.52326/ic-ecco.2021/EL.02>



temperature (OPT) 350 °C. The response value is here ~165%.



**Figure 3. The dependence of the gas response (hydrogen, acetone, 2-propanol, n-butanol, ethanol and ammonia) versus operating temperature for (a) uncoated samples and (b) hydrophobic PV3D3 coated samples.**

### III. EXPERIMENTAL DETAILS

ZnO:Fe nanostructured films were deposited on a pre-cleaned glass substrate microscope glasses (76 mm x 25 mm x 1 mm) by the chemical solutions based approach (SCS) and was reported in a previous work [12]. An ultrathin layer of CuO/Cu<sub>2</sub>O with a thickness of 20 nm was deposited on the ZnO:Fe film with a custom system with DC and RF magnetron and then followed by a heat treatment in the furnace at 420 °C for 30 minutes. The hydrophobic PV3D3 thin films were deposited in a home-made ring-inlet iCVD reactor described in detail in our previous works [3][13][14]. Finally, Au electrodes were deposited on top of the CuO/Cu<sub>2</sub>O/ZnO:Fe heterojunctions coated with a layer of PV3D3 polymer through a meandering mask [15]. For sensor performances a computer-controlled Keithley 2400 sourcemeter at 0.2 V applied bias voltage was used. The details on the sensing experiments can be found in our previous works on gas sensing [16][17].

### ACKNOWLEDGMENT

This research was partially sponsored by the NATO Science for Peace and Security Programme (SPS) [grant number G5634 „Advanced Electro-Optical Chemical Sensors”]. In addition it was partially funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) [grant number Project-ID 434434223-SFB 1461, Project-ID 286471992-SFB1261 project A2, GRK 2154 project P4]. Furthermore, the authors would like to thank the WTSH and the EUSH for partially funding this project BAEW [grant number LPW-E/1.1.2/1486].

### REFERENCES

[1] A. M. Coclite, R. M. Howden, D. C. Borrelli, C. D. Petruczok, R. Yang, J. L. Yagüe, A. Ugur, N. Chen, S. Lee, W. J. Jo, A. Liu, X. Wang and K. K. Gleason, “25<sup>th</sup> anniversary article: CVD polymers: A new paradigm for surface modification and device fabrication,” *Adv. Mater.* vol. 25, pp. 5392-5423, 2013.

[2] M. H. Gharahcheshmeh and K. K. Gleason, “Device fabrication based on oxidative chemical vapor deposition (oCVD) synthesis of conducting polymers and related conjugated organic materials,” *Adv. Mater. Interfaces* vol. 6, pp. 1801564, 2019.

[3] S. Schröder, T. Strunskus, S. Rehders, K. K. Gleason and F. Faupel, “Tunable Polytetrafluoroethylene Electret Films with Extraordinary Charge Stability Synthesized by Initiated Chemical Vapor Deposition for Organic Electronics Applications,” *Sci. Rep.* 9, 2237, 2019.

[4] G. Odian, Principles of polymerization, 4<sup>th</sup> ed., New Jersey: John Wiley & Sons, Inc., 2004, pp.198-349.

[5] W. S. O’Shaughnessy, D. J. Edell and K. K. Gleason, “Initiated chemical vapor deposition of a siloxane coating for insulation of neural probes,” *Thin Solid Films* vol. 517, pp. 3612-3614, 2009.

[6] N. J. Trujillo, Q. Wu and K. K. Gleason, “Ultralow dielectric constant tetravinyltetramethylcyclotetrasiloxane films deposited by initiated chemical vapor deposition (iCVD),” *Adv. Funct. Mater.* vol. 20, pp. 607-616, 2010.

[7] K. K. S. Lau, J. A. Caulfield and K. K. Gleason, “Structure and morphology of fluorocarbon films grown by hot filament chemical vapor deposition,” *Chem. Mater.* vol. 12, pp. 3032-3037.

[8] F. Hu, Q. Cai, F. Liao, M. Shao and S.-T. Lee, “Recent advancements in nanogenerators for energy harvesting,” *Small* vol. 11, pp. 5611-5628, 2015.

[9] M. Minkten, M. Schweichel, S. Schröder, S. Kaps, J. Carstensen, Y. K. Mishra, T. Strunskus, F. Faupel and R. Adelung, „Nanogenerator and piezotronic inspired concepts for energy efficient magnetig field sensors,” *Nano Energy* vol. 56, pp. 420-425, 2019.

[10] G. M. Sessler, Electrets, 2<sup>nd</sup> ed., Berlin Heidelberg New York: Springer, 1987, pp.13-75.

[11] S. Schröder, N. Ababii, O. Lupan, J. Drewes, N. Magariu, H. Krüger, T. Strunskus, R. Adelung, S. Hansen and F. Faupel, „Sensing Performance of CuO/Cu<sub>2</sub>O/ZnO:Fe Heterostructure Coated With Thermally Stable Ultrathin Hydrophobic PV3D3 Polymer Layer for Battery Application,” *Mat. Today Chem.*, in press.

[12] V. Postica, I. Hölken, V. Schneider, V. Kaidas, O. Polonskyi, V. Cretu, I. Tiginyanu, F. Faupel, R. Adelung and O. Lupan, “Multifunctional device based on ZnO:Fe nanostructured films with enhanced UV and ultra-fast ethanol vapour sensing” *Mater. Sci. Semicond. Process.* vol. 49, pp. 20-33, 2016.

[13] S. Schröder, A. M. Hinz, T. Strunskus and F. Faupel, “Molecular insight into real-time reaction kinetics of free radical polymerization from the vapor phase by i-situ mass spectrometry,” *J. Phys. Chem. A* vol. 125, pp. 1661-1667, 2021.

[14] S. Schröder, O. polonskyi, T. Strunskus and F. Faupel, “Nanoscale gradient copolymer films via single-step deposition from the vapor phase,” *Mater. Today* vol. 37, pp. 35-42, 2020.

[15] O. Lupan, V. Cretu, V. Postica, O. Polonskyi, N. Ababii, F. Schütt, V. Kaidas, F. Faupel and R. Adelung, “Non-planar nanoscale p-p heterojunctions formation in ZnxCu1-XOy nanocrystals by mixed phases for enhanced sensors.” *Sens. Actuators B Chem.* vol.230, pp. 832-843, 2016.

[16] O. Lupan, V. Postica, N. Wolff, O. Polonskyi, V. Duppel, V. Kaidas, E. Lazari, N. Ababii, F. Faupel, L. Kienle and R. Adelung, “Localized synthesis of iron oxide nanowires and fabrication of high performance nanosensors based on a single Fe<sub>2</sub>O<sub>3</sub> nanowire,” *Small* vol. 13, pp. 1602868, 2017.

[17] O. Lupan, V. Postica, V. Cretu, N. Wolff, V. Duppel, L. Kienle and R. Adelung, “Single and networked CuO nanowires for highly sensitive p-type semiconductor gas sensor applications,” *Phys. Status Solidi - Rapid Res. Lett.* vol. 10, pp. 260-266, 2016.