Porous Titanium Nitride material for microelectrode based biosensing.

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Context

1. In biosensing for environment or health applications, microelectrode flexible sensors are still very challenging depending on the application target. Several designs are commonly used (either single electrodes or InterDigitated Electrodes), requiring different interface solutions (resistive or capacitive impedance leading to potentiometric or amperometric outputs). The challenges are the sensitivity and selectivity, stability and life time, compatibility with heterogeneous and aggressive environment (in case of biological tissues or polluted water/soils in agrifood). TiN which is bio-compatible, has shown promising properties in case of well controlled surface porosity obtained with specific etching [S. Paul Shylendra, et al, "Titanium Nitride Thin Film Based Low-Redox-Interference Potentiometric pH Sensing Electrodes," Sensors, vol. 21,(1), 2020 ; M. Liu, et al, "A titanium nitride nanotube array for potentiometric sensing of pH," The Analyst, vol. 141, (5), 2016 N. Sun et al., Sputtered titanium nitride films with finely tailored surface activity and porosity for high performance on-chip micro-supercapacitors, Journal of Power Sources 489 (2021) 229406].

2. The thesis in proposed **in continuity with a previous phD work** (Thuy Nguyen, defense in 2023) on flexible smart sensors dedicated to healthcare, and in relation with expertise developed on TiN material within the ERC Neurodiam of L Rousseau. A first proof of concept has been demonstrated on the interest of TiN material for pH sensor electrodes [Porous Titanium Nitride Electrodes on Miniaturised pH Sensor for Foetal Health Monitoring Application, T. Nguyen, B. Journet, H. Takhedmit, G. Lissorgues, DTIP2022]. But **deep material characterization is required** to understand the sensitivity/accuracy improvement in regard to the porosity control in case of porous TiN versus flat TiN. And **the bibliography on this material** is showing an increasing interest on several domains: optics, thermo-optics, electronics [. M. Reed, M. R. Ferdinandus, N. Kinsey, C. DeVault, U. Guler, V. M. Shalaev, A. Boltasseva, and A. Urbas, "Transient Nonlinear Refraction Measurements of Titanium Nitride Thin Films," in Conference on Lasers and Electro-Optics, OSA Technical Digest (online) (Optica Publishing Group, 2016), paper FTu1A.6; A. Calzolari and A. Catellani, "Controlling the TiN Electrode Work Function at the Atomistic Level: A First Principles Investigation," in IEEE Access, vol. 8, pp. 156308-156313, 2020, doi: 10.1109/ACCESS.2020.3017726.]. In addition, we have the clean room facilities in ESYCOM allowing working on the optimization process for porous TiN.

Thesis topic

1. As explained in the context above, there is an increasing interest in the TiN material which was initially only used for thin film coatings. The first target application is pH measurement because the induced porosity of etched TiN, presenting a specific columnar structure, will accelerate H+ ions migration and interaction with the surface at the electrode/electrolyte interface and increase the sensitivity. Other applications can be explored outside electrochemical sensors, in neurosciences for new microelectrode arrays [Ryynänen, T., et al. « Ion beam assisted E-beam deposited TiN microelectrodes —

applied to neuronal cell culture medium evaluation.", Front. Neurosci. 12:882. 2018.], or in energy storage though supercapacitor concepts [Grigoras, K., et al. "Conformal titanium nitride in a porous silicon matrix: a nanomaterial for in-chip supercapacitors.", Nano Energy 26, 340–345, 2016]. If thermo-optic properties appear to be original (to be checked in this thesis), it will also extend the interest of porous TiN towards metamaterial applications.

2. The project will be to **develop new TiN samples with controlled porosity** and to implement such a material **on microelectrodes** for sensing performance assessment. The solution can be easily transferred on flexible substrates based on Esycom previous experience on soft implants. An option will be to **add the wireless transmission** to these sensors **for remote monitoring**, considering a resonant RFID like circuit [P. Marsh et al., "Flexible Iridium Oxide Based pH Sensor Integrated With Inductively Coupled Wireless Transmission System for Wearable Applications," in IEEE Sensors Journal, vol. 20, no. 10, pp. 5130-5138, 15 May15, 2020, doi: 10.1109/JSEN.2020.2970926; M. Smalley, K. Anderson and N. McFarlane, "Towards a Wireless pH-Impedance Sensor System for IoT Applications," 2022 IEEE 65th International Midwest Symposium on Circuits and Systems (MWSCAS), Fukuoka, Japan, 2022, pp. 1-4, doi: 10.1109/MWSCAS54063.2022.9859313]. **Several applications** can be chosen for the final demonstration: healthcare pH blood/sweat/urine monitoring; pH acidity levels in food; pH monitoring in polluted soils or water… depending on the existing collaborations.

3. Expected publications in IEEE Sensors or IEEE J. of Microelectromechanical Systems and patent.

Expected planned work

The work will be divided into several parts corresponding to the main issues :
- Material sample fabrication (optimization process for the porosity control) and full characterization (electrical, optical, chemical composition, electrochemical, thermal…) – mainly Year 1
- Material integration into a biosensing unit (based on existing know-how) – half of Year 2
- Implementation of the biosensor with a wireless transmission module – half of Year 2
- Sensor characterization to demonstrate its functionality and performances – Year 3
- Writing the manuscript & journal paper – half of Year 3

Curriculum

The phD candidate should have a multidisciplinary background with special focus on :
Material sciences, applied physics, micro-technology and electronics.
A personal interest in biosensors will be appreciated.

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Le laboratoire ESYCOM *s'inscrit dans les domaines de l'ingénierie des systèmes de communication, des capteurs et des microsystèmes pour la ville, l'environnement et la personne.*
Les thèmes abordés sont plus spécifiquement :
- *les antennes et propagation en milieux complexes, les composants photoniques - micro-ondes ;*
- *les microsystèmes pour l'analyse de l'environnement et la dépollution, pour la santé et l'interface avec le vivant ;*
- *les micro-dispositifs de récupération d'énergie ambiante mécanique, thermique ou électromagnétique.*