

5A – PTP Innovative Smart System (ISS)

Nano-Capteur

Synthèse chimique de nanoparticules de WO_3 et intégration sur des dispositifs de micro-électronique pour la réalisation d'un capteur de gaz. Evaluation des performances du capteur sous atmosphère contrôlée.

Protocoles des travaux pratiques

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I. CONSIGNES D'EVACUATION DESTINEE AUX ENSEIGNANTS

RAPPEL : Chaque enseignant est responsable de l'évacuation dans l'ordre et le calme de tous les étudiants qu'il a en charge au moment du sinistre.

EN SALLE BLANCHE N°1 :

- ⇒ Évacuer les étudiants par l'issue de secours qui donne directement dans le hall. Ne pas repasser par le sas; ne pas se déshabiller.

EN SALLE BLANCHE N°2 :

- ⇒ Évacuer les étudiants par l'issue de secours qui donne en salle de tests électriques. Ne pas repasser par le sas; ne pas se déshabiller.

Rassembler tous les étudiants par l'issue de secours qui donne en salle de tests électriques.

Effectuer un recensement.

Ne pas réintégrer les locaux sans l'avis des pompiers ou du directeur (ou du responsable technique présent).

II. CONSIGNES DE SECURITE

REPEREZ LES **EQUIPEMENTS DE SECURITE** :

- issues de secours
- douches de sécurité
- extincteurs
- équipements respiratoires autonomes

LE PORT DES **LUNETTES DE PROTECTION** EST **OBLIGATOIRE** POUR :

- nettoyages chimiques (RCA et $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$)
- toutes attaques humides

IL EST **INTERDIT** AUX STAGIAIRES DE TRANSPORTER LES PRODUITS CHIMIQUES d'un poste de travail à un autre.

Gardez présent à l'esprit que :

- le port des gants est obligatoire mais ils ne constituent pas une protection suffisante contre les hautes températures ou les produits corrosifs,
- certains bains dégagent des vapeurs nocives, normalement aspirées par les hottes à flux laminaire,
- les couvre-chaussures rendent parfois le sol très glissant.

III.DIRECTIVES de MANIPULATION

- Pendant toute la durée du « process », le contrôle de la qualité de chaque étape doit être un souci permanent si l'on veut aboutir à un composant final en état de marche, ainsi qu'à un bon rendement sur l'ensemble de la plaquette. Dans ce but, on utilisera, en parallèle avec la plaquette « composants », une plaquette témoin qui permettra de caractériser chaque étape réalisée.
- Attention : les boîtes à plaquettes s'ouvrent en tournant le couvercle dans le **sens** des aiguilles d'une montre.
- Pour prendre une plaquette avec la pince :
 - profiter du méplat dans le cas où la plaquette est dans la boîte
 - pincer à au moins **5 mm du bord** de la plaquette pour réduire le risque de rupture
 - si la plaquette est sur une surface plane, la faire glisser jusqu'au bord pour la saisir plus facilement.
- **Toute plaquette sortant d'un traitement humide doit subir à la fin un rinçage à l'eau D.I. et un séchage mécanique avant d'être rangée dans sa boîte.**
- Un bon rinçage doit inclure un changement de pince, il faut avoir une seconde pince disponible et propre.
- Les becs des pinces ne doivent pas être essuyés (ni sur la blouse, ni sur du papier), ils doivent être rincés à l'eau et séchés à l'azote.
- La fonction des gants est de protéger les composants contre la contamination. Il faut aussi éviter

- de contaminer les gants. Ils ne sont absolument pas une protection efficace aux acides.
- Le plastique des boîtes ne supporte pas les températures supérieures à 250°C. En particulier, la température des plaquettes sortant juste d'un four, laisser celles-ci refroidir environ 20 secondes à l'air libre.
 - Le papier est une source de contamination, faites-en l'usage minimum.

IV. PROCEDURE D'ENTREE EN SALLE BLANCHE

- Laisser les vêtements de ville et les sacs dans la salle de séminaire.
- Six casiers, fermant à clé, peuvent être utilisés dans le SAS pour des objets de valeur.

Entrée en Salle Blanche:

Blouse : blanche : personnel permanent

bleue: stagiaire

verte : visiteur.

Couvre-chaussure : Placer la couture à l'intérieur

Ne poser le pied dans la partie propre qu'une fois chaussé.

Charlotte : Mise à disposition dans le distributeur mural.

Gants latex: 2 tailles mises à disposition dans 2 distributeurs muraux.

Sortie de la salle Blanche :

Blouse : suspendre au cintre numéroté correspondant à chaque binôme.

Couvre-chaussure : déposer dans la partie "USAGES" du coffre.

Charlotte : garder dans la manche de la blouse.

Gants latex: jeter à la poubelle.

Recommandations :

- Veiller à ne pas entrer dans le SAS avec des chaussures de ville boueuses ou mouillées (utiliser le paillasson à l'entrée de l'AIME).
- Limiter le nombre d'objets et de documents qui entrent en salle Blanche (crayon à mine carbone proscrit).

V. INTRODUCTION

Les capteurs de gaz sont des équipements utilisés dans de nombreux domaines (médecine, industrie automobile, industrie agro-alimentaire ...). Ces dernières années, la demande en méthodes de détection de gaz et de mesure de leur concentration a considérablement augmenté. Cet intérêt est essentiellement dû aux considérations environnementales, de sécurité ou de contrôle de procédé, faisant des capteurs de gaz un enjeu important. Dans le domaine de la détection des gaz, il convient de distinguer les analyseurs (instruments d'analyse) et les capteurs chimiques. Les capteurs chimiques possèdent de nombreux avantages, notamment un faible encombrement, une faible consommation énergétique, un faible coût, et un temps de réponse court. Ils peuvent donc être utilisés pour des contrôles de procédés en ligne. Leur principal inconvénient est leur sélectivité. En effet, l'analyse de mélange de gaz nécessite souvent l'emploi de plusieurs capteurs sensibles à l'une ou l'autre des espèces gazeuses. Les capteurs à oxydes métalliques de type semi-conducteurs, tel que l'oxyde de tungstène WO_3 que nous allons utiliser, ont l'avantage de s'intégrer relativement facilement dans des circuits électroniques comme nous le verrons au cours de ce procédé.

OBJECTIFS :

L'objectif est de réaliser un capteur de gaz à base de nanoparticules de WO_3 puis de l'évaluer sous atmosphère gazeuse contrôlée pour en fournir la datasheet. Le procédé se décompose alors en 4 étapes majeures :

- Synthèse des nanoparticules de WO_3
- Elaboration de la puce micro-électronique
- Intégration de la couche sensible de nanoparticules sur la puce
- Caractérisation électrique du capteur sous atmosphère contrôlée

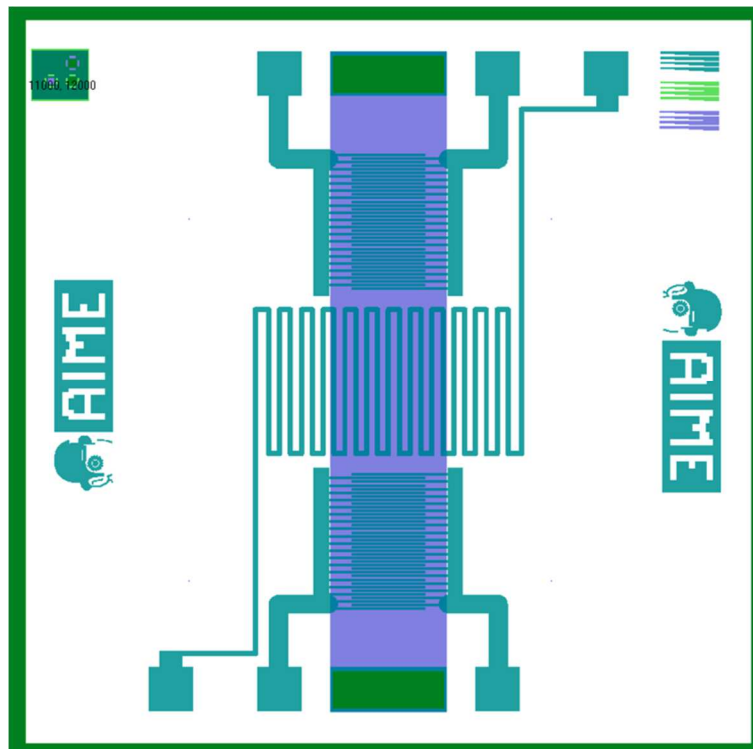
Chaque sous-groupe de 3 binômes devra disposer à la fin d'un capteur dont le fonctionnement aura été validé avant son intégration dans un « smart system ».

VI. FICHE DE PROCESS POUR LA REALISATION DES PUCES

L'intégralité du procédé est donnée ci-après mais seules les étapes effectivement réalisées par les étudiants sont détaillées ; **il s'agit ici des étapes H, I et J uniquement.**

Les puces produites sont constituées de 4 composants :

- Une résistance de chauffage enfouie en polysilicium dopé n
- Une résistance en aluminium pour le chauffage ou la mesure, située en surface
- Deux peignes interdigités qui accueilleront la couche de nanoparticules et qui deviendront alors des résistances sensibles à l'environnement gazeux.



A. OXYDATION DE MASQUAGE

L'épaisseur de l'oxyde de masquage est de 4500 Å environ.

1- Nettoyage avant oxydation

- ☐ **Dégraissage :** Acétone puis eau (à chaud)
- ☐ **Oxydation chimique :** $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ (1/1) 2 min, puis rinçage eau DI
- ☐ **Attaque SiO_2 :** HF dilué 30 s, puis rinçage eau DI
- ☐ **Séchage :** Tournette
- ☐ **Lavage-séchage :** Laveur-sécheur

2- Oxydation thermique humide: cette opération s'effectue en 5 étapes dans le four N°2-2



Température	Temps	Débits
⇐ T = 800 à 1100°C	t = 25 min.	N ₂ = 1 l/min.
⇐ T = 1100 °C	t = 40 min.	H ₂ = 2,7 l/min. O ₂ = 1,5 l/min.
⇐ T = 1100 °C	t = 30 min.	O ₂ = 2,2 l/min.
⇐ T = 1100 °C	t = 10 min.	Ar = 1,5 l/min.
⇐ T = 1100 à 800°C	t = 60 min.	N ₂ = 1 l/min.

B. DEPOT POLY-SILICIUM



Cette opération s'effectue dans le four LPCVD (Low Pressure Chemical Vapor Deposition) n°4-3.

L'épaisseur visée de poly-Si est de 600nm:

Températures	Temps	Débits	Pressions
T= 400°C à 585°C	t = 45 min.	N ₂ = 1 l/min.	p = 1 Torr
T= 585°C	t = 43 min.	SiH ₄ = 50 cc/min. PH ₃ = 2 cc/min.	p=250 mTorr
T= 585°C à 400°C	t = 4 x 2 min.	N ₂ = 1 l/min. : cycles de purges et vides	p=1 Torr

C. DOPAGE DU POLYSILICIUM (de type N)



Le dopage du polysilicium est obtenu par diffusion d'impuretés de phosphore P sur toute son épaisseur.

1- Prédépôt : Cette opération s'effectue en 3 étapes dans le four n°1-1

Température	Temps	Débits
☐ T = 1050 °C	t = 5 min.	N ₂ = 2 l/min. O ₂ = 0.1 l/min.
☐ T = 1050 °C	t = 15 min.	N ₂ = 2 l/min. O ₂ = 0.1 l/min. POCl ₃ = 5 mg/min.
☐ T = 1050 °C	t = 6 min.	N ₂ = 2 l/min. O ₂ = 0.1 l/min.

2- Redistribution : Cette opération s'effectue dans le même four ou dans le four n°1-2 avec les conditions suivantes:

Température	Temps	Débits
☐ T = 1050 °C	t = 5 min.	N ₂ = 2 l/min.

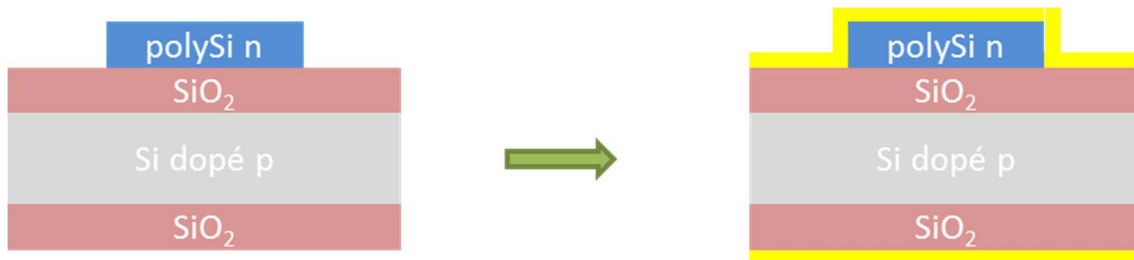
D. PHOTOGRAVURE N°1 : "GRAVURE POLYSILICIUM"



On crée le barreau de polysilicium dopé qui servira de résistance chauffante enfouie sous les capteurs de gaz.

Pour cela on utilise le masque n° 1.

E. DEPOT D'UNE COUCHE D'OXYDE SEC



Cette étape consiste à déposer une couche d'oxyde de silicium de 200 nm d'épaisseur qui isolera électriquement le polysilicium conducteur des pistes d'aluminium des composants en surface. L'épaisseur est optimisée de façon à permettre un bon transfert thermique vers les capteurs de gaz en surface.

F. PHOTOGRAVURE N° 2 : "OUVERTURE CONTACTS"



Afin de pouvoir contacter électriquement la résistance en polysilicium, la couche d'oxyde sec est ouverte à ses deux extrémités, avant l'étape de métallisation.

Cette étape utilise le masque n° 2.

G. METALLISATION



Cette opération consiste à déposer sur la face composant une couche de 500 nm d'aluminium.

Par pulvérisation
cathodique :

⌋ Dépôt	Pression avant dépôt = 10^{-7} mbar
	Pression pendant dépôt = $2 \cdot 10^{-3}$ mbar
	Puissance RF = 250 W
	Distance cible-substrat = 75 mm
	Temp de dépôt = 10 min.

H. PHOTOGRAVURE N° 3 : "GRAVURE METAL"



Cette étape conserve l'aluminium uniquement pour les pistes qui vont définir les composants en surface et les contacts électriques avec ceux-ci, ainsi qu'avec la résistance en polysilicium.

Pour cela on utilise le masque n° 3.

Steps	Conditions
⇨ 0°) Homogenization of etching bath	Sonicate the aluminum etching bath during the following steps.
⇨ 1°) Drying	Oven or hot plate : (120°C) 5 min.
⇨ 2°) Photoresist spin coating	Ref.: Shipley S1813 - Spin coater (4000 rpm, 30 s.)
⇨ 3°) 1st baking	Hot plate (100 °C) 60 s.
⇨ 4°) Alignment - Exposure (5 s.)
⇨ 5°) Development	(20 °C), 15 s.
⇨ 6°) Visual check	Optical microscope
⇨ 7°) 2nd baking	Hot plate (120° C), 45 s.
⇨ 8°) Etching bath	Stop sonication and put each bath on the bench.
⇨ 9°) Aluminium etching	Put the wafer into the etching bath (40vol. H ₃ PO ₄ + 7vol. HNO ₃ + 7vol. H ₂ O). Duration : visual control + extra 30 s.
⇨ 10°) Visual check	Optical microscope
⇨ 11°) Resist removal (2 sides)	Acetone + D.I. water + drying at the centrifuge dryer

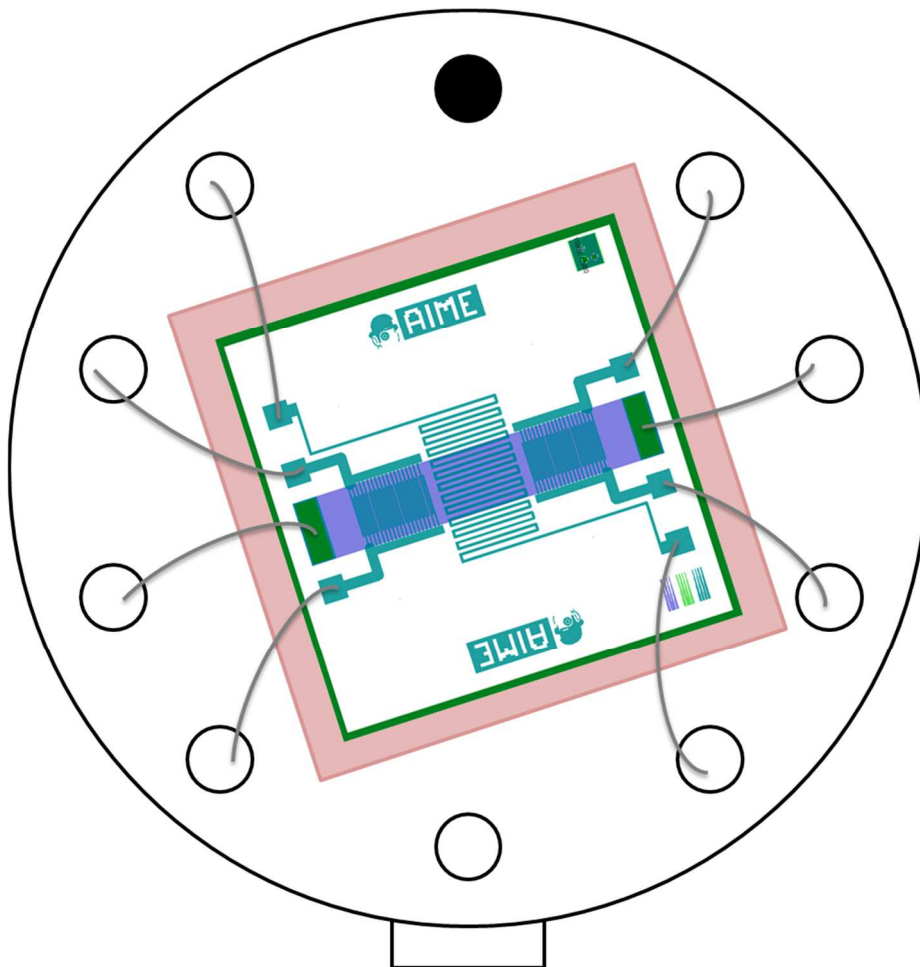
I. METAL ANNEALING

- ⇨ Measure the aluminum layer resistance before and after the annealing (optional)
- ⇨ Measure the aluminum layer thickness on a profilometer.
- ⇨ Annealing is performed in oven N°5-1 according to the following conditions:

Temperature	Duration	Gas - Debits
⇨ T = 400 °C	t = 20 min.	N ₂ + H ₂ (5%)= 1 l/min.

J. ASSEMBLY

- CUTTING of the wafer at the diamond saw.
- SELECTION of the best chips (un-scratched aluminum layer, no short-circuits) by using a binocular.
- ASSEMBLY on a TO5 housing:
 - Glue a glass square plate using a non-conducting epoxy glue,
 - Glue the selected chip onto the glass plate using the same glue,
 - Polymerize the glue at 125°C during 15 min in the oven,
 - Check the good mechanical strength of the assembly.
- Wedge bonding with aluminum-silicon wire (5%, $\phi 25\mu\text{m}$) according to the following picture.



VII. NANOPARTICLES SYNTHESIS

The nanoparticles synthesis operations detailed hereafter are adapted from the scientific publication given in appendix 1. **Safety:** Keep NPs in aqueous solution to limit exposure risks. **Environment:** Rinsing solutions are recovered in a dedicated flask. NOTHING IS DIRECTLY THROWN INTO THE SINK!

A. WO₃ GERMS PREPARATION

Turn on the oven in the Nano room and set it to 180°C.

The first chemical reaction is the hydrolysis-condensation of Na₂WO₄, which is the conjugated base of tungstic acid. Once acidified, the unstable tungstic acid rapidly condenses (loss of a water molecule) and forms a yellow precipitate of nanoscale particles of tungsten oxide (of undefined form and composition).

Steps	Conditions
⇨ 1°) Preparation	Using an automatic pipette, put 5 mL of the Na ₂ WO ₄ solution (0,125 M) into a 100 mL Erlenmeyer. Add a magnetic stirrer bar.
⇨ 2°) Acidification	Under moderate stirring (500 rpm), add in one shot 5 mL of the chloridric acid solution (HCl, 3 M).
⇨ 3°) Reaction	Let the reaction complete under stirring for 5-10 min.
⇨ 4°) Transfer	Transfer the whole suspension (not the stirrer bar) into a centrifugation tube with a minimum amount of D.I. water (~3x 2mL).
⇨ 5°) Centrifugation	Make sure all the tube weight the same before putting them into the rotor in a way the latter keeps being equilibrated. Centrifuge at 5000 rpm during 3 min.
⇨ 6°) Washing	Remove the supernatant (D.I. water with dissolved NaCl and excess HCl), and repeat the washing of the powder by centrifugation with 10mL of D.I. water (at least once, and maximum twice if required).
⇨ 7°) Storage	Keep the yellow powder at the bottom of the centrifugation tube for the next step.

B. GROWTH OF THE WO₃ NANORODS

Since the oven will be at 180°C and we use water as solvent, we need to perform the next reaction into a special vessel that hold high pressure (an hydrothermal bomb, see picture).

The speed and duration of centrifugation steps can be adapted to the visible decantation of the suspension, as well as the number of washing steps.



Steps	Conditions
⇐ 1°) Weight of Na ₂ SO ₄	Weight 5g directly into the Teflon beaker of the hydrothermal bomb.
⇐ 2°) Germs transfer	Transfer the germs from the centrifugation tube to the Teflon beaker by using 3x 2mL of D.I. water sampled with an automatic pipette.
⇐ 3°) Mixing	Slowly stir the mixture with a spatula to break the sulfate salt crystal formed after water addition.
⇐ 4°) Closure	Correctly assemble the hydrothermal bomb and tightly close it with its special wrench.
⇐ 5°) Annealing	Put the bomb into the oven at 180°C during 1h. Meanwhile, clean the vessel and the bench for next groups.
⇐ 6°) Cooling down	Take out the bomb and let it cool down few minutes on a metal bench. Finish cooling it down to room temperature under a water flow in the sink (~10 min).
⇐ 7°) Opening	Open the bomb and transfer the sample into another centrifugation tube. Use 3x 5mL of D.I. water to help you transfer the entire solid.
⇐ 8°) Centrifugation	Check the weight of the tubes and put them all in the centrifuge. Centrifuge at 12000 rpm during 4 min.
⇐ 9°) Washing	Remove the supernatant (water and dissolved Na ₂ SO ₄), and repeat the washing of the white nano-powder with 15 mL of D.I. water (at least 2 times).
⇐ 10°) Storage	Transfer all the nanorods into a small vial using 3x 2mL of D.I. water. Correctly label your sample.

VIII. NPS SELECTIVE DEPOSITION BY DIELECTROPHORESIS

Equipment

AC voltage source / oscilloscope / connectors / NPs sample.



DEPOSITION Protocol

Steps	Conditions
1° Sonication	Put the sample in a sonication bath for 1 min.
2° Connection	Connect one of the interdigitated electrodes to the AC generator (remove the protection cap). Make sure the generator is on standby. Place it horizontally above an empty beaker.
3° Droplet formation	Use the micropipette to form a small droplet of the NPs solution on top of the chip (around 5 μ L).
4° Dielectrophoresis	Polarize the electrodes with a sinus voltage at 100 kHz (amplitude of 10 V _{cc}). Run the dielectrophoresis for 60s. Let the voltage ON during the next 2 steps!
5° Washing	Wash the droplet off the chip with D.I. water using the automatic pipette (1 mL, twice).
6° Drying	Absorb the excess of water with a clean dry tissue from the side of the chip. Be careful to not break the aluminum bonding! Compressed air can also be useful for that operation.
7° Standby	Turn off the polarization voltage.
8° Visual check	Use an optical microscope to try to detect if the deposition of a nanoparticle layer is effective or not (you can also use the dark field mode).

First electrical characterization of the sensors

Gas sensors are now ready to be electrically characterized and selected for gas detection evaluation. The goal is to find at least one functional chip for the 3 groups.

Two measurement bench are available in the characterization room to test the behavior of the resistors (Poly and Al), and of the sensitive NPs layer.

Steps	Conditions
⇒ 1°) Drying	Remove carefully the protection cap and put the gas sensor in the oven at 125°C for 5 min to remove traces of water. After drying, always let the cap on.
⇒ 2°) LabTracer2 I(V) curve	<ul style="list-style-type: none">• Measure the I(V) curve of the sensitive layer at Room Temp. (max 20V),• Measure the I(V) curve of the Poly resistor (max 15V) at R.T.,• Measure the I(V) curve of the Al resistor (max 10V) at R.T.,
⇒ 3°) High temperature behavior	Use a DC voltage generator to work at high temperature; connect it to the Poly resistor and choose appropriate voltages (max 15V). Measure the I(V) curve of the sensitive layer at different temperatures to understand how it behaves.
⇒ 4°) Working temperature	Select one or two interesting working temperatures you will use for the gas detection evaluation.

IX. MEASUREMENT UNDER CONTROLLED ATMOSPHERE

We now want to measure the variation of the sensitive layer resistance in the presence of a specific gas at one given concentration in synthetic dry air. This will be recorded at different working temperature. The bench is equipped with 3 gas lines: pure synthetic dry air (80% N₂ - 20% O₂), ammonia (NH₃) at about 0.1% in dry air, and ethanol (C₂H₆O) at about 0.1% in dry air.

Test bench initialization

- Connect the gas sensor on its support in the gas chamber (align the ergo with the red mark). Remove the protection cap and close the chamber,
- Open the gas line gate on the wall,
- Turn on the measurement apparatus and the computer.
- Launch the Labview program and set the following parameters:
 - Check the polarization voltage is correctly set at 20V.
 - Choose the destination folder for data recording. (First enter a random file name that must be deleted by hand after selection of the folder)

Gas sensor characterization

Temperature adjustment: use the B channel of the Kethley (DC voltage source mode, max 1.5W and max 15V). Measure the injected current through the “Hi” channels (use “Display” and “MODE” buttons to select it). **Be careful: do not change the voltage range while injecting current or you may damage the Poly resistor. Also, avoid rapid variation of voltage to reduce the risk of damaging thermal shock (go back slowly to zero...).**

Estimation of the chip surface temperature will be done by using the variation of aluminum resistivity with it (cf appendix 2). To do it correctly, you need to measure the R_{Al} value at room temperature first, and then at the working temperature. Their ratio will help estimating the working temperature.

Gas detection: you can now define your own protocol to evaluate the response of the gas sensor to one specific gas. You will find an example of previously performed measurement in appendix 3. It is of high interest to do it with several gas, at different temperature (**Be careful: do not forget to change the filename after each measurement!**)

After analysis/treatment of the data, you will be able to establish the complete datasheet of your gas sensor.

WO₃ synthesis protocolAn Inorganic Route for Controlled Synthesis of W₁₈O₄₉ Nanorods and Nanofibers in Solution

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In this work, we describe a simple inorganic route for synthesis of monodispersed W₁₈O₄₉ nanorods with dimensional control in the quantum confinement regime. The single-crystalline W₁₈O₄₉ nanorods can be prepared into stable colloidal solutions, or assembled into fibrous and/or paper forms by tuning process parameters. The important role of Na₂SO₄ salt in the synthesis has been demonstrated. This inorganic route should be feasible for large-scale production of low-dimensional nanostructured W₁₈O₄₉.

In recent years, transition metal oxides have received increasing attention in the synthesis of nanostructured materials.^{1–9} Among them, a significant fraction of the work has been devoted to fabrication of one-dimensional (1D) tungsten oxides (WO_{3–x}, $x \geq 0$) due to their many known

applications such as in electrochromic windows, optical devices, secondary batteries, gas sensors, and photocatalysts.^{2,3} In particular, monoclinic W₁₈O₄₉ (or WO_{2.72}) is of great interest owing to its unusual defect structure and promising properties in the nanometer regime.^{4–10} Nonetheless, most of the synthetic work for this 1D nanostructure reported is limited to high-temperature methods with either vapor or vapor–solid processes.^{4–9}

For the large-scale production, wet chemical methods need to be further developed. Most recently, colloidal W₁₈O₄₉ nanorods with excellent quality had been synthesized with W(CO)₆ at 250–270 °C in the presence of Me₃NO·2H₂O and excess oleylamine, followed by various treatments in organic solvents.¹⁰ In addition to this organic route, it would also be desirable to search for inorganic alternatives using low-cost precursors and solvents. Herein, we describe a facile inorganic route for synthesis of uniform W₁₈O₄₉ nanorods or nanofibers in aqueous solution. This novel method is based on treating freshly prepared H₂WO₄·xH₂O in the presence of Na₂SO₄ salt under hydrothermal conditions at 160–200 °C for 2–24 h.

In a typical synthesis, 10 mL of hydrochloric acid (3 M) was added dropwise to 10 mL of sodium tungstate solution (0.125 M) under stirring. A light yellow precipitate of amorphous tungstic acid appeared gradually. The mixture was vigorously stirred for 15 min followed by centrifugation (3000 rpm, 5 min), after which deionized water (20 mL) and a certain amount of sodium sulfate (0–20 g) were immediately added to the solid precipitate. The mixture was then vigorously stirred for 1–2 h (a slurry form was observed after 1 h when 20 g of Na₂SO₄ was used); the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 160–200 °C for a period of 2–24 h. After reaction, the autoclave was then cooled to room temperature under tap water. The final product was harvested by centrifugation and washed with deionized water (several times) and pure alcohol (one time) to remove Na₂SO₄ and any other possible remnant. The obtained products were characterized with scanning electron microscopy (SEM, JSM-5600LV), trans-

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- (1) (a) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446. (b) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353. (c) Rao, C. N. R.; Cheetham, A. K. *J. Mater. Chem.* **2001**, *11*, 2887. (d) Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. *Chem. Eur. J.* **2002**, *8*, 29. (e) Kovtyukhova, N. I.; Mallouk, T. E. *Chem. Eur. J.* **2002**, *8*, 4355.
- (2) (a) Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **2000**, *60*, 201. (b) Turyan, I.; Krasovec, U. Q.; Orel, B.; Saraidorov, T.; Reisfeld, R.; Mandler, D. *Adv. Mater.* **2000**, *12*, 330. (c) Qu, W. M.; Wlodarski, W. *Sens. Actuators, B* **2000**, *64*, 42. (d) Li, X. Z.; Li, F. B.; Yang, C. L.; Ge, W. K. *J. Photochem. Photobiol., A* **2001**, *141*, 209. (e) Santato, C.; Odziemkowski, M.; Ulmann, M.; Augustynski, J. *J. Am. Chem. Soc.* **2001**, *123*, 10639.
- (3) (a) Millner, T.; Neugebauer, J. *Nature* **1949**, *163*, 601. (b) Pfeifer, J.; Badaljan, E.; Tekula-Buxbaum, P.; Kovács, T.; Geszti, O.; Tóth, A. L.; Lunk, H. J. *J. Cryst. Growth* **1996**, *169*, 727. (c) Qi, H.; Wang, C.; Liu, J. *Adv. Mater.* **2003**, *15*, 411. (d) Li, Y. B.; Bando, Y.; Golberg, D.; Kurashima, K. *Chem. Phys. Lett.* **2003**, *367*, 214. (e) Liu, Z.; Bando, Y.; Tang, C. *Chem. Phys. Lett.* **2003**, *372*, 179.
- (4) Zhu, Y. Q.; Hu, W.; Hsu, W. K.; Terrones, M.; Grobert, N.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M.; Terrones, H. *Chem. Phys. Lett.* **1999**, *309*, 327.
- (5) York, A. P. E.; Sloan, J.; Green, M. L. H. *Chem. Commun.* **1999**, 269.
- (6) Hu, W. B.; Zhu, Y. Q.; Hsu, W. K.; Chang, B. H.; Terrones, M.; Grobert, N.; Terrones, H.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *Appl. Phys. A* **2000**, *70*, 231.
- (7) Gu, G.; Zheng, B.; Han, W. Q.; Roth, S.; Liu, J. *Nano Lett.* **2002**, *2*, 849.
- (8) Hudson, M. J.; Peckett, J. W.; Harris, P. J. F. *J. Mater. Chem.* **2003**, *13*, 445.
- (9) Li, X. L.; Liu, J. F.; Li, Y. D. *Inorg. Chem.* **2003**, *42*, 921.

- (10) Lee, K.; Seo, W. S.; Park, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 3408.

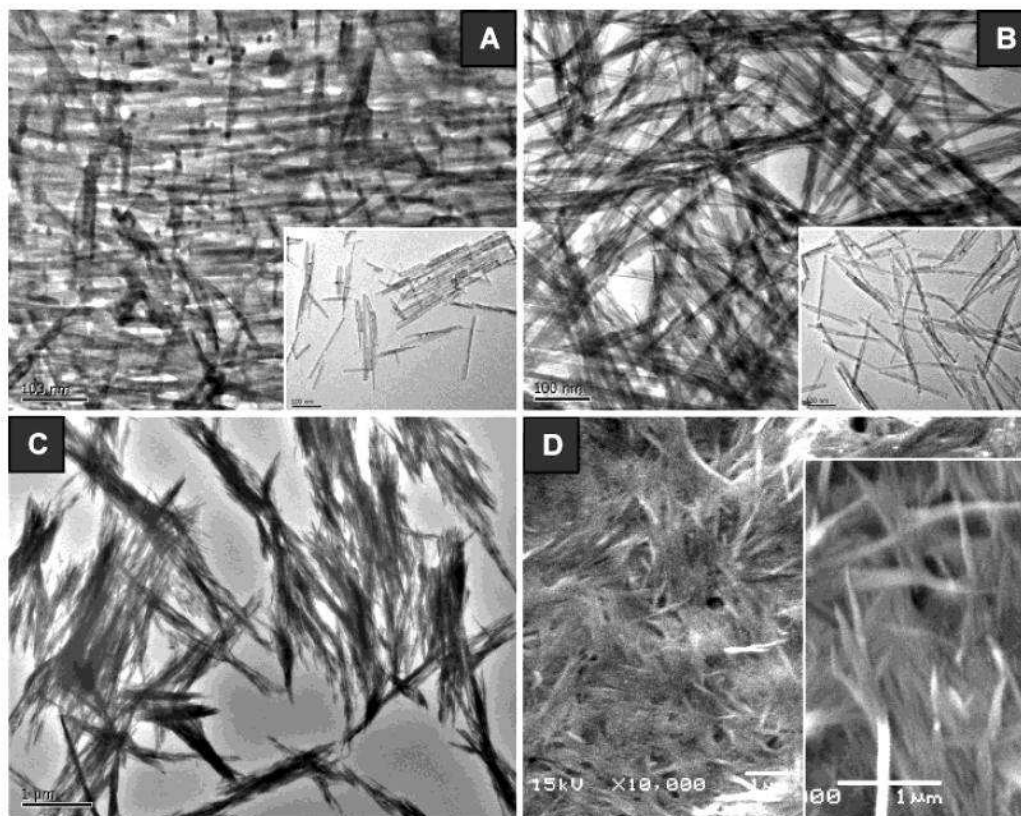


Figure 1. $W_{18}O_{49}$ nanorods and fibers synthesized with 20 g of Na_2SO_4 salt at 180 °C for different reaction times: (A) 2 h (TEM images), (B) 8 h (TEM images), (C) sample from part B with additional 16 h in deionized water (i.e., 8 + 16 h, TEM image), and (D) 16 h (SEM images).

mission electron microscopy and electron diffraction (TEM/ED, JEM-2010F, 200 kV), high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy (HRTEM/EDX, Philips-CM200 FEG, 200 kV), and powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu $K\alpha$ radiation).¹¹ The room temperature photoluminescence spectra of $W_{18}O_{49}$ nanorods were obtained with a fluorescence spectrometer (LS-55 Perkin-Elmer) with xenon (300 nm; 150 W pulsed xenon lamp) as an excitation source.

Figure 1 shows various $W_{18}O_{49}$ products synthesized as a function of reaction time in this work. After only 2 h, single-crystalline $W_{18}O_{49}$ nanorods in 100% morphological yield had readily formed with the diameter and length in the ranges 3–10 and 100–250 nm. Due to their small sizes, the individual tiny rods easily form parallel aggregates, such as raftlike arrangement (inset, Figure 1A) or “monolayer” settlement largely through interactions of their highly unsaturated sidewalls.¹² The continuous growth is evidenced in samples with longer reaction times. In Figure 1B, the nanorods have increased their diameter and length to 3–15 and 150–300 nm, respectively. The diameters reported here are only nominal owing to the rod aggregation, which will be addressed by the HRTEM technique (Figure 2C) shortly. It should be mentioned that this type of aggregation is mainly physical, and monodispersed nanorods can be obtained simply with more solvents in ultrasonic treatments: colloidal solutions of $W_{18}O_{49}$ nanorods in acetone solvent are stable

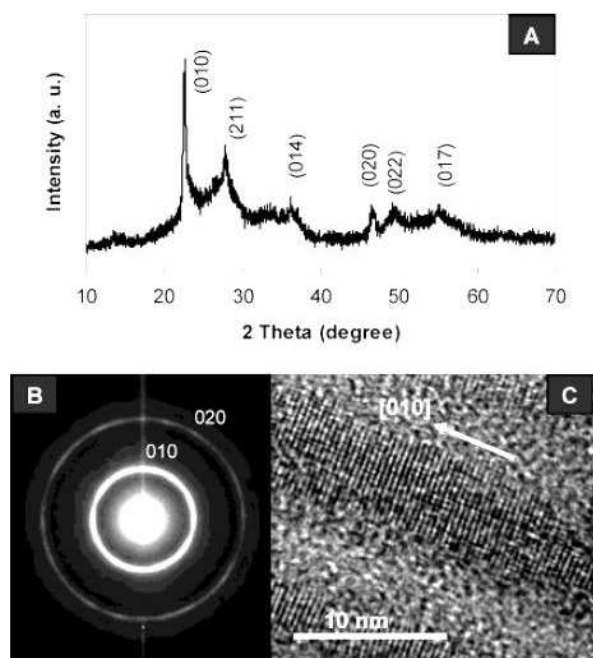


Figure 2. (A) XRD pattern for $W_{18}O_{49}$ nanorods, (B) ED pattern for randomly distributed $W_{18}O_{49}$ nanorods, and (C) HRTEM image for $W_{18}O_{49}$ nanorods (from Figure 1B).

for days. For example, the diameters of monodispersed $W_{18}O_{49}$ nanorods are on average 6.9 ± 1.6 nm (2 h, Figure 1A) and 7.3 ± 2.1 nm (8 h, Figure 1B), respectively. More permanent connectivity among these nanorods can be generated by hydrothermal treatment. In Figure 1C, for example, fiberlike $W_{18}O_{49}$ was prepared from the same sample used in Figure 1B, but with an additional heat treatment in deionized water at 180 °C for 16 h. This fibrous morphology is well preserved even with extensive ultrasonic treatments with surfactants (e.g., cetyl-trimethylammonium-bromide had

(11) (a) Lou, X. W.; Zeng, H. C. *J. Am. Chem. Soc.* **2003**, *125*, 2697. (b) Liu, B.; Zeng, H. C. *J. Am. Chem. Soc.* **2003**, *125*, 4430.

(12) (a) Shi, H.; Qi, L.; Ma, J.; Cheng, H. *Chem. Commun.* **2002**, 1704. (b) Kwan, S.; Kim, F.; Akana, J.; Yang, P. *Chem. Commun.* **2001**, 447. (c) Yu, S. H.; Antonietti, M.; Colfen, H.; Giersig, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2356.

been tested in this work): our TEM investigation indicates that the $W_{18}O_{49}$ nanorods had attached to one another forming fiber bundles through their side crystal planes during the treatment. Longer reactions (e.g., 16–24 h, 20 g of Na_2SO_4) result in the formation of fibrous $W_{18}O_{49}$ with the length up to a few micrometers. Figure 1D displays two SEM images of the “ $W_{18}O_{49}$ paper” prepared from a prolonged synthesis: details on the fiber length and “paper” texture can be obtained from the inset. Our TEM results reveal that the paperlike morphology is also composed of aggregated shorter nanorod bundles (separable in solvents). Although the length of nanorods can be varied by reaction time, the diameter of individual nanorods shows much weaker time dependence.

In Figure 2A, a representative XRD pattern for our as-synthesized tungsten oxide nanorods is displayed. All the main peaks can be indexed undisputedly to monoclinic $W_{18}O_{49}$ (JCPDS card 05-0392).^{4–10} Consistent with general features of nanomaterials,¹ the overall diffraction intensity is weak, and peak broadening is pronounced. Diffraction peaks of $(0k0)$ are stronger compared with the rest, indicating that the $\langle 010 \rangle$ is the major growth direction. EDX analysis gives an O/W atomic ratio of 2.6 ± 0.2 , which is in good agreement with the theoretical value of $W_{18}O_{49}$. Furthermore, the ED pattern in Figure 2B shows two strong $(0k0)$ rings, confirming that the $\langle 010 \rangle$ is indeed the preferential growth direction.¹⁰ Figure 2C presents an HRTEM image of nanorods with the diameters 3–7 nm. The lattice spacing along $\langle 010 \rangle$ is determined to be $d_{010} = 0.38 \pm 0.01$ nm, in excellent agreement with the reported lattice constant of monoclinic $W_{18}O_{49}$.^{4–10}

It is apparent that the sodium sulfate plays a crucial role in controlling the 1D growth and substoichiometric phase.¹³ Without adding this salt, only the hexagonal phase of WO_3 (verified by XRD; JCPDS card 33-1387)¹⁴ is formed; the products are showed as elongated hexagonal platelets and irregular nanoparticles. In Figure 3, the effect of salt is further demonstrated. With 2.5 g of Na_2SO_4 , the hexagonal WO_3 still coexists with monoclinic $W_{18}O_{49}$ nanorods. With 3.5 g of the salt, phase-pure $W_{18}O_{49}$ can be achieved, but 100% rod morphology can only be obtained with 5 g of Na_2SO_4 added. Above 5 g, however, further modification on rod morphology is not pronounced. Other stable inorganic salts such as $NaCl$ and $NaNO_3$ had also been tested in this work, but no obvious effects were observed. We have also carried out syntheses at 160 and 200 °C. Reactions at 160 °C (16–24 h) produce more monodispersed short $W_{18}O_{49}$ nanorods (about 100 nm in length) but are generally mixed with nanoparticles. On the other hand, reactions at 200 °C (16 h) give large fiberlike rod bundles with the length up to a few micrometers owing the more permanent interconnectivity generated at high temperature.

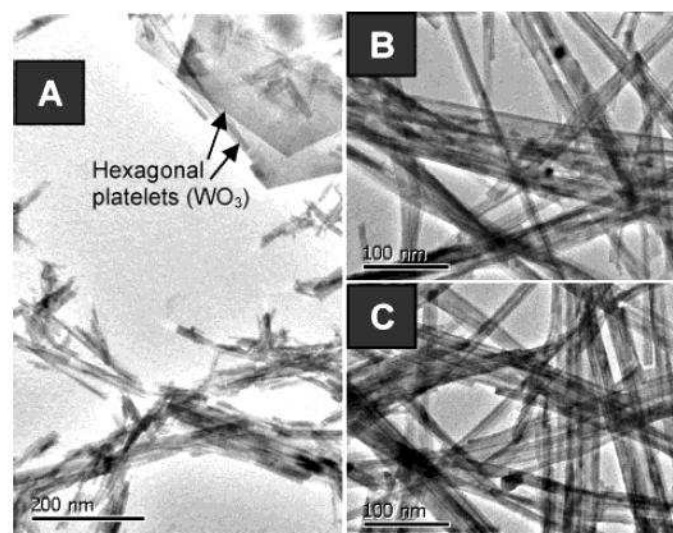


Figure 3. $W_{18}O_{49}$ nanorods synthesized at 180 °C for 16 h with different amounts of Na_2SO_4 salt: (A) 2.5 g, (B) 5 g, and (C) 10 g.

The room-temperature photoluminescence (PL) emission spectra of the $W_{18}O_{49}$ nanorods generally exhibit two emission maxima over the studied wavelength range, which is quite similar to a previously reported pattern for $W_{18}O_{49}$ nanorods synthesized via an organic route,¹⁰ although the energy levels of the two emission peaks are less separate owing to different measurement conditions. For example, the higher energy peaks of the sample series of Figure 1 appear at 3.43 eV (360.6 nm; 4 h), 3.39 eV (364.9 nm; 8 h) and 3.38 eV (366.8 nm; 16 h) respectively, while the lower energy peaks are essentially constant at around 2.95 eV (ca. 420 nm). The slight blue-shift observed in the samples synthesized with a shorter reaction time indicates that the nanorods prepared in this work are entering the quantum confinement regime, as their size effect has been noticed.

Though little is known about the general growth mechanism of 1D $W_{18}O_{49}$, the crucial role of sodium sulfate has been clearly demonstrated in the current case. For instance, sulfate ions might adsorb on side surfaces of the nanocrystals or modify the ionic strength of reactant species in solution,¹⁵ preventing the rods from radial enlargement. Furthermore, these anions could also be involved in possible redox reactions in forming $W_{18}O_{49}$ under hydrothermal conditions. Further investigation on these mechanistic aspects is needed.

In summary, we have developed a simple inorganic route to prepare monodispersed $W_{18}O_{49}$ nanorods with dimensional control in the quantum confinement regime. The single-crystalline $W_{18}O_{49}$ nanorods can be prepared into stable colloidal solutions, or be assembled into fibrous and/or paper forms by tuning process parameters. The important role of Na_2SO_4 salt in the synthesis has been demonstrated. This aqueous route should be feasible for large-scale production of low-dimensional nanostructured $W_{18}O_{49}$.

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(13) (a) Wang, X.; Li, Y. *J. Am. Chem. Soc.* **2002**, *124*, 2880. (b) Guo, C. W.; Cao, Y.; Xie, S. H.; Dai, W. L.; Fan, K. N. *Chem. Commun.* **2003**, 700. (c) Hsu, W. P.; Ronquist, L.; Matijević, E. *Langmuir* **1988**, *4*, 31. (d) Garg, A.; Matijević, E. *J. Colloid Interface Sci.* **1988**, *126*, 243.

(14) (a) Komaba, S.; Kumagai, N.; Kato, K.; Yashiro, H. *Solid State Ionics* **2000**, *135*, 193. (b) Kumagai, N.; Kumagai, N.; Umetzu, Y.; Tanno, K.; Ramos, J. P. P. *Solid State Ionics* **1996**, *86–88*, 1443.

(15) Xu, R.; Zeng, H. C. *J. Phys. Chem. B* **2003**, *107*, 926.

Aluminum resistivity as a function of temperature.

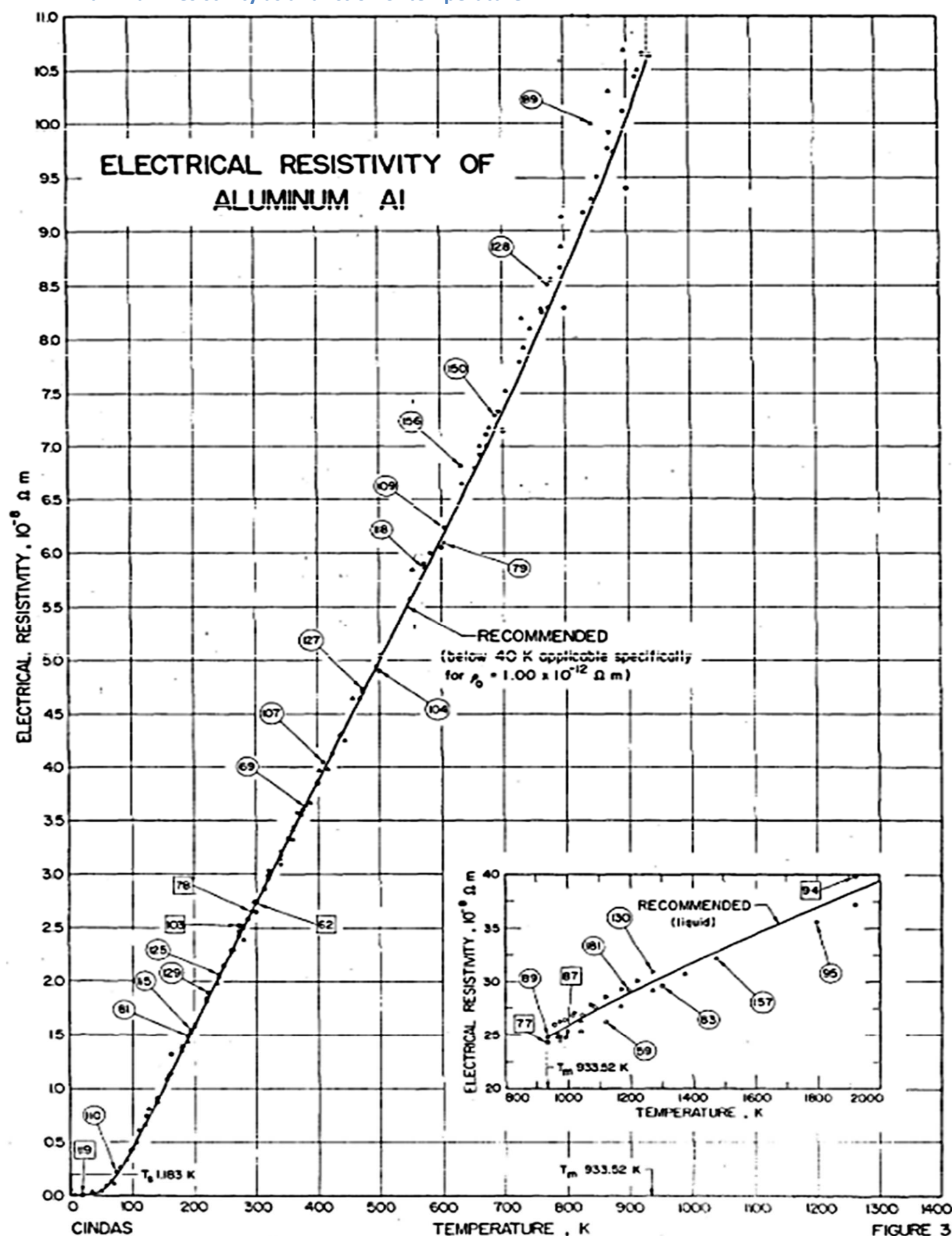


FIGURE 3

Characterization protocol for gas sensors (proposition)

Perform a characterization of your gas sensor around the following temperatures: 120°C, 180°C, 250°C.

At each temperature:

- Create a first file in which you will record what happens when you increase the temperature with no gas flow. Wait until the resistance is roughly stabilized. Keep the chips at this stabilized temperature for the following steps.
- Create a second file in which you will record the sensor response to gas. The protocol can be the following:
 - Start measurement during 15s without any gas flow
 - dry air during 2 min
 - ethanol during 2 min
 - dry air during 2 min
 - ethanol during 2 min
 - dry air during 2 min
 - NH₃ during 2 min
 - dry air during 2 min
 - NH₃ during 2 min
 - dry air until stabilization

