UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF NANOCRYSTALLINE THICK FILM GAS SENSORS

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

To My Beloved: Mina, Zahra & Reza

My Mother Masoomeh & My Mother-in-Law Mansooreh

who their loves never end to me

and to the

Memories of My Father Ali, & My Father-in-Law Gholamreza

God Bless Them

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Chairman: Mohd Nizar b Hamidon, PhD

Faculty: Engineering

In the last three decades along with growing industries and development of cities, many pollutants have entered into the environment cycle. Some resultants of these contaminations can be felt as air pollution. Now, many cities across the world have been equipped with the databases to collect and analyze the information related to air quality and to give the index of air pollution known as API. In order to record and monitor the pollution, some of those databases use advanced equipment and instrument which are very expensive and need regular overhaul and maintenance. However, some databases are equipped with simpler gas detectors, so-called solid state gas sensors.

Nowadays, many types of solid state gas sensors, employed different techniques of fabrication, are released in the market. One of those techniques is known as Thick Film Technology which has proved to be very promising and low cost option to fabricate gas sensors for gas analyzers, but some problems still are

associated to their efficiency such as deficient of selectivity, influence of humidity, cross sensitivity, response time, and power consumption. The main goal of this doctoral thesis is to develop a nanocrystalline metal oxide thick film gas sensor using print screen technology having fast response time and highly sensitive to air contaminants.

The fabricated gas sensor consists of a heater, an electrode, and a sensitive film onto an alumina substrate, which can stand up to high firing temperature during fabrication and operation. To fabricate the sensitive paste, tin dioxide (SnO_2) and tungsten trioxide (WO_3) were used as the base powders. Meanwhile, platinum, silver, and yttria (Y_2O_3) were used as additives and dopings. Finally, types of alcohol (ethyl alcohol, isopropanol, and methanol), hydrocarbon (xylene, isobutane), ketones (acetone), mixture of inorganic gases (exhaust fumes), and wood smoke were applied to the sensors for measurement.

Fabrication of the sensitive paste has brought the development of a novel vehicle binder in the organic phase of the paste. The novel binder fulfills the screen printing criteria in which can be prepared very fast, having less additional material with at least one month shelf life. Crystallite size of sensitive powder of the sensors was measured using XRD analysis, showing sizes less than 30 nm and 20 nm for metal oxide phase and metal additives, respectively. Low dependency of WO_3 sensors doped with Y_2O_3 to humidity was observed. Sensitivity of fabricated sensors in the presence of applied gases was compared to some commercial sensors and higher sensitivity was observed. The $0.9WO_30.1Y_2O_3$ sensor (WY-90) shows to be very sensitive to organic solvents

compared with sensitivity of TGS2620 (Alcohol Sensor). The $0.98SnO_2 0.02Pt$ sensor (SnPt-980) shows to be more sensitive with faster response time to organic solvents and truck exhaust gas than the commercial sensors of TGS2602 (Air Quality Taguchi Sensor), TGS3870 (Methane and Carbon Monoxide), and TGS4160 (Carbon Dioxide). It shows a response time as low as 15 seconds in the presence of 500 ppm exhaust gas compared to 28 seconds response time of TGS2602.

Since the sensor is equipped with a heater element, it can operate at different working temperatures and produce different sensing signal in the presence of different gases or solvents, lead to have a selective gas sensor. Also, the approach of screen printing fabrication eases the fabrication of an array of four individual gas sensors with a very thin metal oxide and catalyst layer, using pulse laser ablation deposition (PLAD) technique. The results show that the response time of the array is significantly decreased to as low as 5 seconds in the presence of 200 ppm acetone.

Abstrak Tesis dihadapkan kepada Senat Universiti Putra Malaysia untuk keperluan kelayakan ijazah Doktor Falsafah

PENGEMBANGUNAN PENDERIA GAS FILEM TEBAL NANOKRISTALIN

Oleh

MOHAMMAD HADI NEZHAD SHAHROKH ABADI

Disember 2010

Ketua: **Mohd Nizar b Hamidon, PhD**

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Dengan perkembangan industri dan pembangunan bandar semenjak tiga dekad kebelakangan ini banyak bahan pencemar telah memasuki kitaran alam sekitar. Ada di antara bahan pencemar ini yang boleh dirasai kehadirannya sebagai pencemaran udara. Banyak bandar di seluruh dunia kini telah dilengkapi dengan pangkalan data untuk mengumpul dan menganalisis informasi berkaitan dengan tahap kualiti udara dan berfungsi untuk memberikan indeks pencemaran udara (API) untuk merekod dan memantau pencemaran tersebut. Sesetengah pangkalan data menggunakan peralatan dan instrumentasi yang maju tetapi berkos tinggi serta memerlukan penyelenggaraan yang kerap. Tetapi terdapat juga pangkalan data yang dilengkapi dengan penderia gas yang lebih ringkas iaitu penderia gas berkeadaan pejal.

Kini, terdapat banyak jenis penderia gas berkeadaan pejal yang menggunakan pelbagai teknik pembuatan yang terdapat di pasaran. Salah satu teknik ini

dikenali sebagai Teknologi Selaput Tebal dimana ianya terbukti sebagai antara pilihan yang meyakinkan serta berkos rendah untuk fabrikasi penderia gas. Namunpun begitu ia masih mempunyai masalah berkaitan dengan kecekapan seperti kekurangan di dalam pemilihan, pengaruh kelembapan, kepekaan rentas, masa tindakbalas dan penggunaan tenaga. Objektif utama tesis doktorat ini ialah untuk membangunkan "penderia gas selaput tebal nanokristal logam teroksida" dengan menggunakan teknologi pencetak skrin yang mempunyai masa tindakbalas yang pantas dan sangat peka terhadap unsur pencemar udara.

Penderia gas yang telah dibina mengandungi gelung pemanas dan filem sensitif di atas alumina dimana ia boleh bertahan pada pemanasan suhu tinggi ketika proses pembuatan dan semasa beroperasi. Untuk pembuatan bahan sebatian sensitif penderia gas, tin dioksida (SnO_2) dan tungsten trioksida (WO_3) digunakan sebagai bahan asas. Manakala, platinum, perak, dan yttria (Y_2O_3) digunakan sebagai bahan penambah dan pengdopan. Akhir sekali, jenis-jenis alkohol (ethyl alcohol, isopropanol, dan methanol), hydrocarbon (xylene, isobutane), ketones (acetone), campuran gas bukan oraganik (gas ekzos), dan asap daripada kayu telah digunakan terhadap penderia sebagai pengukuran.

Pembuatan bahan sebatian sensitif telah membawa kepada pembentukan pembantu pengikat terkini di dalam fasa sebatian organik tersebut. Pembentukan pembantu pengikat terkini yang memenuhi kriteria pencetakan skrin dimana ia boleh disediakan dengan pantas, serta kurang penggunaan bahan tambahan dan boleh digunakan dalam tempoh sebulan. Saiz hablur halus sensitif daripada penderia telah diukur dengan menggunakan analisis XRD, dimana ia

menunjukkan saiz kurang daripada 30 nm dan 20 nm untuk fasa oksida logam serta bahan tambahan logam. Kurangnya kebergantungan penderia WO_3 (yang didopkan dengan Y_2O_3) terhadap kelembapan telah diperhatikan. Kadar kejituan gas penderia dengan kehadiran gas telah dibandingkan dengan beberapa penderia komersil yang sangat peka terhadap kehadiran gas. Penderia $0.9WO_30.1Y_2O_3$ (WY-90) menunjukkan kadar kepekaan yang tinggi terhadap bahan pelarut organik berbanding dengan penderia TGS2620 (Penderia Alkohol). Penderia $0.98SnO_20.02Pt$ (SnPt-980) menunjukkan kadar kepekaan yang tinggi dengan masa tindakbalas yang lebih singkat terhadap bahan pelarut organik dan gas daripada ekzos kenderaan berbanding penderia komersil TGS2602 (Air Quality Taguchi Sensor), TGS3870 (Methane and Carbon Monoxide), dan TGS4160 (Carbon Dioxide). Ia menunjukkan masa tindakbalas masa serendah 15 saat dengan kehadiran 500 ppm gas ekzos berbanding dengan 28 saat respon masa oleh TGS2602.

Disebabkan penderia ini dilengkapkan dengan elemen gelung pemanas, ia boleh beroperasi pada suhu yang berbeza-beza dan menghasilkan isyarat deria yang berbeza bergantung kehadiran kepada jenis gas dan bahan pelarut. Ini menunjukkan penderia gas ini bersifat selektif. Pendekatan teknik pembuatan pencetak skrin juga telah digunakan bagi fabrikasi empat penderia gas individu di dalam satu susunan dengan oksida logam dan lapisan pemangkin yang sangat nipis menggunakan teknik Pulse Laser Ablation Deposition (PLAD). Keputusan menunjukkan bahawa masa tindakbalas susunan empat penderia gas tersebut jatuh secara signifikan sebanyak 5 saat dengan kehadiran 200 ppm acetone.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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