

ENABLING MEMS CHEMICAL MICROSENSOR ARRAYS FOR TRACE ANALYTE DETECTION

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Abstract: We describe the development of a conductometric gas microsensor technology that combines, in an optimized manner, nanostructured sensing films, MEMS microhotplate array platforms, and artificial neural networks signal processing. Individually addressable microelements, including varied semiconducting oxides, are temperature modulated to produce analytically rich data streams that allow recognition of low concentration target analytes in background mixtures. This brief report emphasizes: 1) recently developed selection and processing methods for incorporation of high performance sensing materials on the MEMS platforms, 2) special operational modes and data acquisition approaches for ensuring good signal quality while maximizing information content, and 3) signal analysis techniques that include preprocessing routines and advanced recognition algorithms.

Keywords: array, conductance, MEMS, metal oxide, microhotplate, neural networks, temperature

1. INTRODUCTION

The detection of low concentration analytes in varied gas phase mixtures represents a broad and challenging problem for sensor researchers. Success in this endeavor, however, could provide critical measurement tools for diverse application areas that include emissions monitoring, space exploration, health diagnostics and homeland security. The sensors would have the greatest impact if they were reliable, tunable for differing conditions, and readily adaptable for network deployment. In this brief paper we describe recent advances that have been implemented to enhance the ability of conductometric microsensor arrays developed at the National Institute of Standards and Technology (NIST) to detect target chemicals at trace concentrations. The advances relate to new film processing steps developed for use with our MEMS device platforms, improved selection methods for sensing material quality and orthogonality, and programming cycles that probe a greater range of temperature-dependent interactions. The technology has been used to detect a variety of toxic industrial chemicals (TICs) and chemical warfare simulants (CWSs) at concentrations ranging from ~ 500 ppt (nmol/mol)

to ~ 100 ppm ($\mu\text{mole/mol}$) in air-based backgrounds that include interferences. New signal preprocessing techniques have also been introduced to allow near-real time monitoring.

2. EXPERIMENTAL

The NIST array technology combines $100 \mu\text{m}$ microhotplate elements with CMOS compatibility (see Fig. 1), nanostructured sensing films, and artificial neural network (ANN) signal processing to realize tiny, application-tunable devices that consume very little power [1]. The platforms (now expanded from 4 to 16 elements)

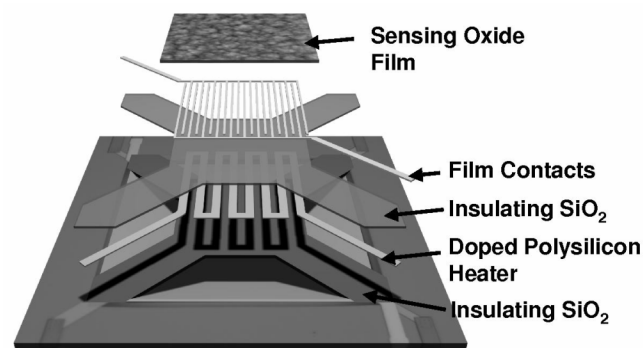


Fig. 1 Schematic structure of a single microhotplate element, which can be realized by top-side micromachining of silicon.

continuously measure the conductance of sensing films (4 unique compositions in the current version) deposited on the separate micromachined microhotplates while each is individually programmed through rapid temperature-programmed sensing (TPS) cycles. Fig. 2 shows a recently developed TPS cycle that acquires analytically rich data streams from the array elements (containing information on temperature dependent surface reactions and adsorption/desorption processes at the different types of sensing films). ANN/statistical routines then process the complex data streams [2] to detect target compounds.

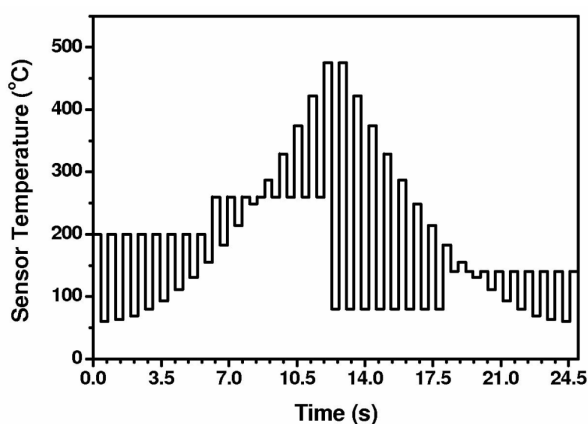


Fig. 2 An example of a 25-second temperature program that has been employed to recognize low concentrations of toxic industrial chemicals in complex backgrounds.

Semiconducting metal oxide sensing films, such as SnO_2 and TiO_2 , are localized (self-lithographically) on the microhotplates by thermally activated chemical vapor deposition (CVD), after micromachining [3]. The structures of the CVD films can be altered by changing the temperatures of the microhotplate elements used during deposition [4]. Other types of nanostructured materials have also been incorporated on the array elements to enhance sensitivity and selectivity [5,6]. X-ray photoemission spectroscopy (XPS) measurements made prior to deposition have indicated that our micromachining process (tetra-methyl ammonium hydroxide, TMAH) produces Si surface contamination on the Pt electrodes. Ion beam etching is now used to remove the Si prior to the sensing oxide CVD, leading to better Pt-oxide

contact, and the ability to make thinner oxide films (and use various nanostructured oxides) with higher sensitivity and stability.

3. RESULTS

Microarray elements operated in the TPS mode produce dense data sets from each sensing material for analyte recognition. Fig. 3 shows an example of temperature-programmed data from a thin, highly sensitive SnO_2 microsensor, and associated ANN probabilities arising from the array data, which indicate detection of the CWS cyclohexyl methyl methylphosphonate (CMMP) at 700 ppt.

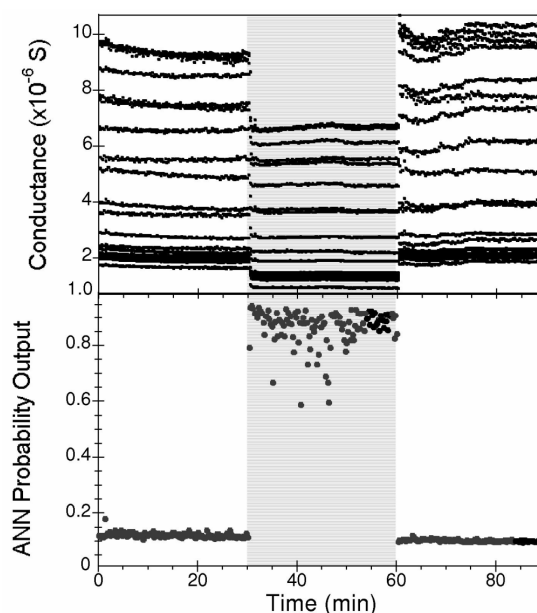


Fig. 3 Temperature-varied conductance isotherms from a single thin CVD SnO_2 sensing film and the neural networks probabilities derived from this and related data for detection of a chemical warfare simulant (CMMP – presented to the sensor in the gray portion of the time axis) at 700 ppt in 40% RH air.

The selection of film thicknesses and compositions for a specific detection problem (that can have different target analytes and backgrounds) has been improved by employing statistical correlation measures to assess orthogonality/similarity of the chosen materials, and by visualizing the microarray response using dimensionality reduction techniques to determine whether sufficient analytical information is

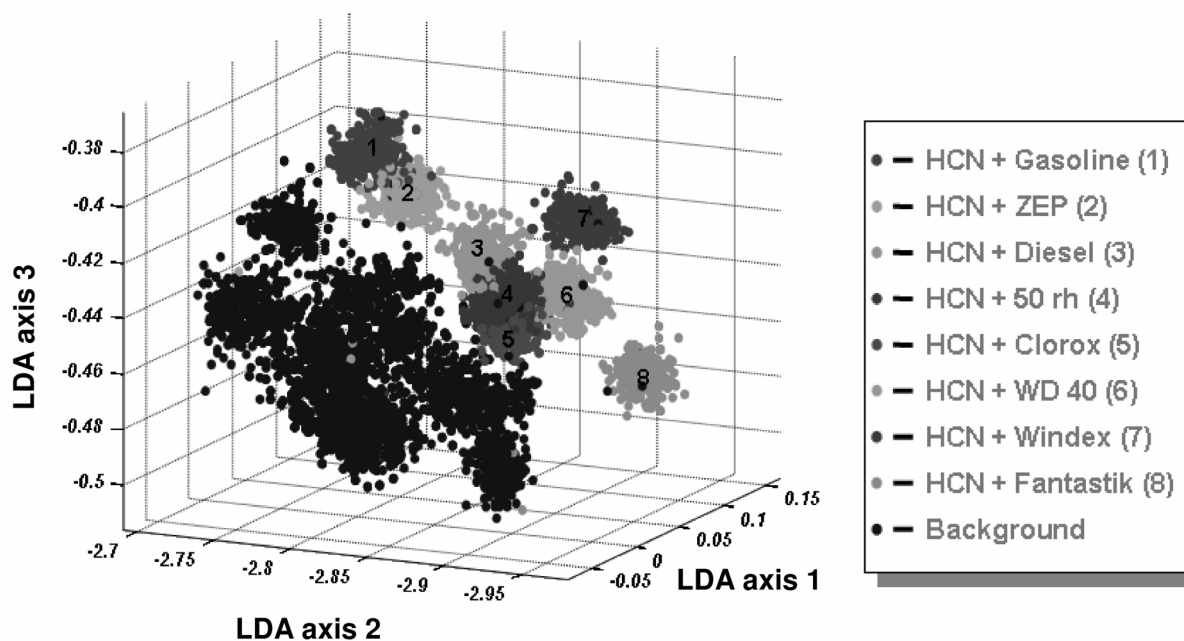


Fig. 4 Linear discriminant analysis indicating that temperature-programmed conductance data from multiple oxide sensing films allow discrimination of HCN-containing exposures (lighter, numbered clusters) compared to non-HCN exposures (dark clusters) that include varied interferences.

available for species recognition. The linear discriminant analysis plot in Fig. 4 shows that HCN exposures are readily discriminated from non-HCN exposures with TPS data from two oxide types, each operated in the data-rich TPS mode.

While our prior work on trace detection relates largely to chemical warfare agent (CWA) detection in simple air backgrounds [7], our improved microarray sensors and signal processing techniques have allowed us to achieve detection capabilities on enlarged sets of hazardous chemicals under more varied background conditions (humidities, temperatures) and compositions (6 TICs with 7 individual interferences, 5 CWSs with 2 interferences). Demonstrated detection schemes include in-sector ANN training/validation, as well as pretrained classification schemes with preprocessing techniques (see Fig. 5) [8], which have been instrumental in moving our technology toward near-real time performance.

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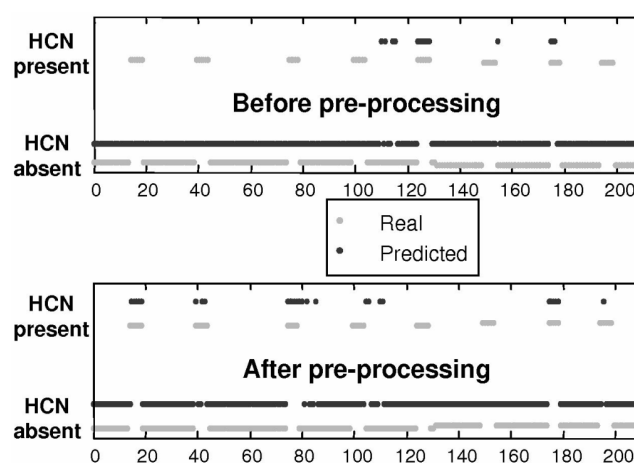


Fig. 5 Post-training *k*-nearest neighbor (KNN) recognition of HCN (50 ppm) exposure periods illustrating the significant improvement in detection under a spectrum of background conditions when a recently devised data pre-processing algorithm is applied.

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