Cross-reactive graphene and ZnO chemical vapor sensors for precise discrimination

Chen Shi¹, Huixian Ye², Dimitris E. Ioannou¹, Hui Wang², Qiliang Li¹

- ¹ Department of Electrical and Computer Engineering, George Mason University, Fairfax, Virginia 22030, United States
- ² Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 20003, China qli6@gmu.edu

Abstract:

We report a study of cross-reactive analysis based on graphene and ZnO chemical vapor sensors for precise discrimination. Transient features were extracted by exponential fitting to the sensor response curve at room temperature. Three fitting parameters were extracted for each adsorption/desorption process. A classification method based on two sets of transient features was utilized to improve the selectivity and accuracy of chemical sensing. The algorithm was first verified in the monolayer graphene sensor. The results indicated that the chemical discrimination can be significantly improved by the transient feature analysis. To further improve the performance, two different gas sensors (monolayer graphene and ZnO thin film) were prepared to perform the transient feature analysis. Consequently, two sets of testing results were obtained and the extracted transient features were applied in a cross-reactive analysis to enhance discrimination precision.

Key words: metal oxide, graphene, transient feature analysis, cross-reactive analysis

Introduction

As far back as 1965 there are reports of semiconductor materials exhibiting electrical conductivities that are strongly affected by ambient gases and vapors. In recent years chemiresistor technology has been used to develop gas sensors for many applications. The most commonly investigated materials include metal oxides, 2D materials and polymers. [1-3]

Benefited from the development of material science and fabrication technology, numerous methods have been proposed to improve the performance of chemical resistive gas sensors. However, most chemical resistive gas sensors are limited to high operation temperature and display poor selectivity due to the nature of chemical adsorption. The solution of high selectivity and high accuracy of gas sensors at room temperature requires a paradigm shift in sensor design.

In this work, cross-reactive analysis has been studied in graphene and ZnO chemical vapor sensors for precise discrimination. Transient features have been extracted from the gas sensing curves and applied to the feature analysis. It was verified in the monolayer

graphene sensor that transient feature analysis can improve the chemical discrimination significantly. [4] Following this observation, two sets of testing results were obtained and the transient features were extracted from the two different gas sensors (monolayer graphene and ZnO thin film). They were applied in a cross-reactive analysis to enhance the discrimination precision.

Device fabrication

ZnO thin film was deposited on the sapphire substrate by sputtering. The sputtering was conducted in reactive atmosphere with O_2 flow. After deposition, an optimized annealing was applied to engineer the morphology of the film and enhance the gas sensing property. For the fabrication of the graphene sensor, 4" monolayer graphene on SiO_2/Si was purchased from Graphenea. This is a bi-dimensional material produced by CVD and transferred to a circular substrate of SiO_2/Si by a wet transfer process.

Interdigitated comb pattern of Ti/Au metal stack was deposited on both sensors to form the contact and bonding pad.

Device test

A bubbler test system was utilized for our tests. The investigated chemicals (including acetone, mesitylene, toluene, and xylene) are solutions at ambient condition. The vapors are transported by Ar₂. Vapor concentration can be calculated based on the vapor pressure. Further dilution can be controlled by adjusting the gas flow rate of target gas and dilute gas (Ar₂). The mixed gas flows to the test chamber through a solenoid valve. The devices were measured by an Agilen semiconductor parameter analyzer (4156C).

Transient feature analysis and crossreactive analysis

The typical response curve to chemical vapors is shown in Fig. 1. It includes the response part and recovery part (inlet). They are analyzed separately and can be fitted with a single exponential time-function, with time constants related to the characteristic times of the adsorption and desorption process. The fitting data is also shown in Fig. 1.

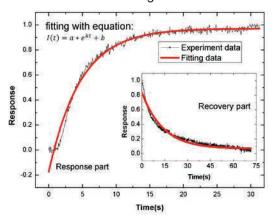


Fig. 1. Typical cyclic response curve of chemical resistive vapor sensor and its exponential fitting.

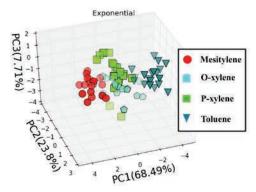


Fig. 2. PCA transient feature analyzing with exponential fitting

For each cycle of gas sensing test, two sets of exponential parameters can be extracted. Then the PCA method is conducted to reduce the dimensions of fitting coefficients to the same level of conventional coefficients and extract the

most meaningful and informative factors from the original fitting coefficients. The classification accuracy of PCA transient feature analysis increased from 64% to 92%. A similar process can be also applied to the concentration analysis. The response curve to different concentrations of acetone observed in ZnO thin film testing is shown in Fig. 3. It is noticed that 50s is required to get a stable signal. However, transient features can be extracted in 30s and fast accurate detection is possible.

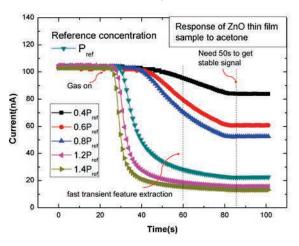


Fig. 3. ZnO thin film gas sensor responds to different concentration of acetone (only the response part is shown in figure).

Conclusion

In this work, the cross-reactive analysis based on transient features in graphene and ZnO chemical vapor sensors was studied. The improvement of the chemical discrimination benefited from cross-reactive analysis of two sets of transient features obtained from the graphene and the ZnO thin film sensors.

References

- [1] Meng, Fan-Li, Zheng Guo, and Xing-Jiu Huang, Graphene-based hybrids for chemiresistive gas sensors, TrAC Trends in Analytical Chemistry 68, 37-47 (2015); doi: 10.1016/j.trac.2015.02.008
- [2] Nallon, Eric C., et al. "Chemical discrimination with an unmodified graphene chemical sensor." ACS Sensors 1.1, 26-31 (2015);doi: 10.1021/acssensors.5b00029
- [3] Gusain, Abhay, et al. Flexible NO gas sensor based on conducting polymer poly [N-9'-heptadecanyl-2, 7-carbazole-alt-5, 5-(4', 7'-di-2-thienyl-2', 1', 3'-benzothiadiazole)] (PCDTBT), Sensors and Actuators B: Chemical 239, 734-745 (2017); doi: 10.1016/j.snb.2016.07.176
- [4] Ye, Huixian, et al. Optimization of the Transient Feature Analysis for Graphene Chemical Vapor Sensors: A Comprehensive Study, *IEEE Sensors Journal* 17.19, 6350-6359 (2017); doi: 10.1109/JSEN.2017.2740942