NO_x Adsorption on SnO_2 Nanoparticles: Dynamics of the Surface Reactions in Correlation with SnO_2 Sensing Properties

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Abstract

This work reports a FTIR study of NO_X adsorption on semiconductor tin oxide nanosized particles in relation with the sensing properties of the material. The chemical reactions are monitored *in situ* simultaneously with the electrical conductivity variations. A different dynamics was found between the main surface reactions and the changes in the SnO_2 electrical conductivity. Thanks to our investigation technique developed in earlier works, the chemical reactions solely responsible for the variations of the SnO_2 electrical conductivity have been tentatively determined.

Introduction

Semiconductor chemical gas sensors detect gases through the variations of the semiconductor electrical conductivity induced by chemical reactions or interactions occurring at the semiconductor surface under gas adsorption. The correlation between the surface reactions and the changes in the electrical conductivity is not always straightforward because the reactions can be multiple generating several kinds of surface chemical species differently linked to the surface. Moreover, apparent discrepancies may be observed between the dynamics of the reactions and the response time of the sensor.

In previous works [1,2], we have proved that Fourier transform infrared (FTIR) spectroscopy is a high-performance tool to follow *in situ* the chemical reactions at the surface of semiconductor nanosized particles and to simultaneously monitor the induced changes in the electrical conductivity. This technique is applied to investigate the adsorption of NO_X on the SnO_2 surface in order to identify the specific reaction(s) responsible for the NO_X detection by SnO_2-based chemical sensors.

Results and discussion

The infrared surface spectrum of SnO_2 shows that, under the first adsorption of NO_X on the fresh SnO_2 surface, the newly formed prominent surface species are nitrate groups coordinated in the bidentate and bridged geometries. Additionally, a broad negative band is due to the decrease of the free carrier absorption generated by a decrease of the electrical conductivity. An infrared analysis versus time shows that the decrease of the free electron density, that is the decrease of the electrical conductivity is almost completed within the first 2 minutes under NO_X adsorption. Then, after the first 2 minutes, nitrate groups continue to form with practically no change in the electrical conductivity. The formation of nitrate groups is a relatively slow process whereas changes in the electrical conductivity are quite fast. Therefore, nitrate groups cannot be responsible for the response of the sensor to NO_X. Nitrate groups are not reversible under desorption and thus the SnO_2 surface remains contaminated after the first NO_X adsorption/desorption cycle.

During subsequent NO_X adsorption/desorption cycles under similar conditions, the surface reactions and their dynamics are different from those observed during the first cycle. No formation of new nitrate groups is detected. The species formed under the subsequent NO_X adsorptions are mainly gaseous species (NO_2, N_2O_4) and are eliminated by evacuation. Concomitantly, reversible effects and smaller changes in the free electron absorption are observed. It is proposed that the formation of (NO_X^-) nitrosyl anion, resulting from the adsorption of NO_X on surface oxygen vacancies, would trap free electrons into localized states, thus leading to a decrease of the electrical conductivity. The dynamics of NO_X^- formation is compatible with the response time of the sensor.

Perspectives

The ultimate role of FTIR spectroscopy in the optimization of chemical gas sensors is to identify the surface reactions responsible for the reversible reactions generating the reversible changes in the electrical conductivity. This is achieved through several gas adsorption/desorption cycles to check the reversibility of the reactions and through an analysis of the reactions dynamics to check the compatibility with the sensor response.

References

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2. M.-I. Baraton and L. Merhari, *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*, **3**, 733-742 (2005).