



Stepwise improvement of (hetero-) polysiloxane sensing layers for CO₂ detection operated at room temperature by modification of the polymeric network

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ABSTRACT

Gas sensors based on the work function read out of (hetero-) polysiloxane sensing layers containing primary amino groups ($-NH_2$) can be used for the detection of CO₂. The sensing mechanism is assumed to be an acid/base reaction between primary amino groups and CO₂. In literature, both a bicarbonate formation and a carbamate formation are discussed. To investigate the reaction with CO₂, different polymers based on modified polysiloxanes are examined. It is shown that the CO₂ response of work function type sensors can be systematically improved by modifying the polymeric network on the one hand (adjoining primary amino groups) and by increasing the hydrophobicity on the other hand. The findings summarized in this paper indicate the possibility for new ambient temperature CO₂ sensors with short response (<1 min) and recovery times (<5 min), a high long-term stability (months to years) as well as a high SNR (signal noise ratio) of ca. 25 (exposure from 400 ppm up to 4000 ppm CO₂). Furthermore, the fast establishment of the chemical equilibrium is remarkable when humidity is changed in atmosphere.

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1. Introduction

In recent years, various CO₂ sensitive materials have been investigated, such as carbonates (Li₂CO₃ [1,2], BaCO₃ [3], Na₂CO₃ [4], SrCO₃ [5]), metal oxides [6,7] (e.g. CuO-BaTiO₃ [8]) and hydroxylapatites [9] as well as CO₂ sensitive materials containing amino groups, such as monomeric amines [10], polymeric imines [11], hydrazines [12], triazines [13], and organically modified silicates, also named siloxanes [14,15]. A budding progress was the detection of CO₂ with work function change measurements at room temperature by investigating siloxanes which contained amino groups [16,17]. It could be verified that tertiary amino group systems (a nitrogen atom is threefoldly linked to carbon atoms), like CPT (Cyanopropyltriethoxysilane) and NNDE (N,N-diethyl-3-aminopropyl-trimethoxysilane), show no work function response when exposed to variations in CO₂ concentration (400–4000 ppm). Primary amino group systems like AMO (3-aminopropyltrimethoxysilane), however, do: the work function measurements of siloxanes revealed short response times (few minutes) and signal noise ratios of 10–15 when exposed to 4000 ppm CO₂ (bad air) at room temperature, beginning at a background concentration of 400 ppm CO₂ (typical in normal air) [16,17]. A comparison of different transducer principles for CO₂ sensing polysiloxanes can be found in [18].

According to literature [19,20], the primary amino group (RNH₂, R= moiety molecule) can react with CO₂ in two different ways (Fig. 1). On the one hand, a single primary amino group can form bicarbonate; on the other hand, two primary amino groups can form a carbamate complex (cf. Fig. 1). The former reaction is effected with H₂O at higher temperatures, whereas the latter is formed without any H₂O, and starts at lower temperatures. Additionally, a direct conversion of bicarbonate to carbamate (or vice versa) is possible by separating (or adding) H₂O. Literature rates especially the last mechanism (change of the chemical equilibrium between bicarbonate and carbamate) as preferable reaction mechanism in work function type sensors: within the first month after preparation, the amount of primary amino groups decreases; bicarbonate and strong indications for carbamate groups could be found using Raman, DRIFT-MIR and NMR analysis [16]. Five weeks after preparation, only 24% N–H (primary amino group) but 76% NH₄⁺ (bicarbonate, carbamate) were detected. A stable CO₂ response was observed after this time which is attributed to the establishment of a chemical equilibrium. Further evidence is a higher CO₂ response under dry conditions, a higher CO₂ response with increased hydrophobicity, a rising t_{90} -time with increased temperature, as well as a changed CO₂ response with intermittent heat pulses (adjustment of the chemical equilibrium).

Since the interaction mechanism is a specific interaction between primary amino groups and CO₂ (and H₂O), only marginal cross-sensitivity to different volatile organic compounds (VOC) is expected for the work function change. This assumption could be proven by measurements of a polysiloxane sensing layer exposed

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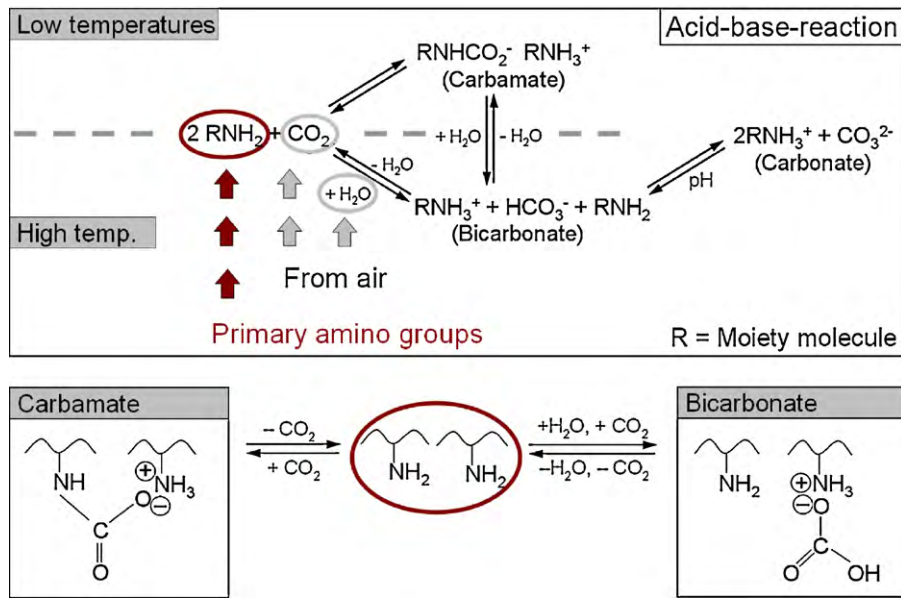


Fig. 1. Possible reaction paths of CO₂ with primary amino groups [19,20].

to small concentrations of acetone (0.5 and 5 ppm), pentanal (0.1 and 1 ppm) and methylamine (0.2 and 2 ppm) [17].

The purpose of this paper is to enhance a stepwise change of the polymeric network (which evokes a change of the chemical equilibrium) in order to assist an eventual carbamate formation, and thus, to improve the CO₂ work function response measured by Kelvin probe. The results can be used for work function type sensors such as the Floating Gate FET (FGFET) [21,22], which modulate the source drain current via the field effect. Advantages associated with these device types are low costs, small size, free choice of the gas sensitive material, the ability to detect signals of some mV and the possibility to operate the sensor at room temperature.

2. Experimental

High quality Al₂O₃-ceramics (99.6%), covered with sputter deposited gold, served as substrate for all variants of sensor materials. On top of this electrode, the gas sensitive material (polysiloxane) was deposited by spin coating of hydrolyzed monomers. To establish layers with varying thicknesses, different rotation velocities were used. After the spin coating process the sensitive layers are temporarily stored in normal air for 2 h to remove solvents and thereby to reach a gel state. The sol-gel condensation is then further completed in N₂ atmosphere for 16 h at a temperature of 120 °C. The tempering leads to a formation of –O–Si–O–Si– bridges and removes the residual H₂O as well as the residual alcohol. Thus a solid state sensitive layer is formed.

Investigated sensitive materials (cf. Fig. 2) are AMO and mixtures of AMO with PTMS (propyltrimethoxysilane). The mixture of PTMS adds hydrophobic characteristics to the hydrophilic AMO. Additionally, AE-AMO (N-(2-aminoethyl)-3-aminopropyltrimethoxysilane), which is characterized by an additional secondary amino group (2RNH), is investigated. Furthermore, mixtures of A3EO (3-aminopropyltriethoxysilane) with A1EO (3-aminopropyltrimethoxysilane) are deposited to reach a lower degree of polymerization and, simultaneously, a higher degree of hydrophobicity. The difference between the monomers AMO and A3EO is a methoxy- and ethoxy-group, respectively, which disappear after hydrolysis. Therefore, both exhibit the same structure after polymerization. Another variant is A2EO (3-aminopropylmethyldiethoxysilane), which assures the formation

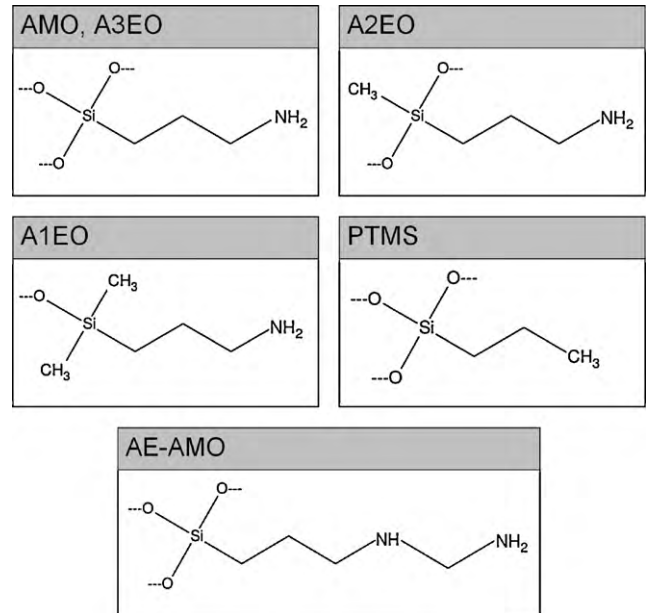


Fig. 2. Schematics of the investigated polysiloxanes (after polymerization).

of a linear structure of the polysiloxane. Therefore, more adjoining primary amino groups are supposed to be present, as they are necessary to form carbamate. Furthermore, the polymerized A2EO exhibits a high hydrophobicity as well as a high density of primary amino groups. However, not a solid, but a high viscous fluid state (absence of a three-dimensional network) can be reached. In this regard a thickness measurement is quite difficult.

To test for a sufficient degree of condensation of the sensitive layers, AMO/PTMS 70:30 (v/v) was subjected to a ²⁹Si NMR-spectroscopy. Fig. 3 shows the different possibilities of a single, double, or triple condensation. The result features on the one hand a majority of triple condensates RSi(OSi)₃ (75.8%) and a minority of single condensates RSi(OSi)₁(OH)₂ (1.8%) on the other hand. According to [23], a degree of condensation of about 91% could be ascertained, which characterizes a regular manufacturing process of the sensitive layers.

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