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A study on the Langmuir adsorption for quartz crystal resonator based low pressure CO_2 gas sensor

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ABSTRACT

Quartz Crystal Resonator (QCR) has been proved to be effective for CO_2 gas sensing, however, the mechanism of this sensing process remains unclarified. This paper proposes an innovative modeling for a QCR-based CO_2 gas sensor. The proposed modeling is based on the Langmuir Adsorption Theorem and the Sauerbrey equation of QCR. The Langmuir Adsorption Theorem assumes that a monolayer of gas molecules is formed at the maximum gas concentration while each adsorbate molecule is assumed to take only one active site on the adsorbent surface. Therefore, the Sauerbrey equation is modified by combining Langmuir Adsorption Theorem and then the effect of both surface concentration and Langmuir constant are investigated and analyzed. Different from traditional analysis, the proposed modeling works well on not only the linear relationship between CO_2 concentration and frequency shift at low CO_2 concentration but also the non-linear saturation stage at higher CO_2 concentration. Moreover, a lab experiment is carried out to verify the Langmuir-Sauerbrey adsorption modeling. Surface concentration constant and Langmuir constant are retrieved from the experiment and considered as material properties for gas sensing capability. The proposed modeling could also be applied to most QCR-based gas sensor, in which physical adsorption is mainly involved. Additionally, determination of surface concentration constant and Langmuir constant will benefit the understanding of many other gas sensing process.

1. Introduction

It is reported that more than 80% of U.S. energy are coming from fossil fuels, which are mostly consumed by industries and automobiles and turned into greenhouse gas. Among them, CO_2 is the most common one and accounts for the biggest proportion [1]. As a result, CO_2 sensing has been attracting more and more attention for its importance on gas turbines, automobile internal combustion engines, steel refining industries and detrimental effects on the global warming problem. For decades, a number of researchers have been making efforts to improve the sensitivity and selectivity of CO_2 sensors. Tatsumi Ishihara *et al* have applied particular oxide capacitor consisting of $BaTiO_3$ as CO_2 sensor based on capacitor change and the sensitivity to CO_2 is strongly dependent on the certain oxide that mixed with BaTiO3 [2–4]. Masayuki Nagai *et al* developed a CO_2 gas sensor based on comprising porous hydroxyapatite ceramics in 1988, which has fundamental sensor characteristics [5]. S.A. Waghuley *et al* have applied chemically synthesized conducting polymer polypyrrole (PPy) as CO_2 gas sensor by sensing the increased resistance of the material due to CO_2 molecules formed weak bonds with π-electrons of PPy [6]. In 2013, Desmond Gibson *et al* successfully applied infrared light as CO_2 sensor which can be implemented by wireless and portable deployment [7].

In recent years, the emergence of quartz crystal resonator (QCR) has provided a good alternative to gas sensor due to its high stability, high accuracy and fast response. Laura Baldini *et al* have designed a QCR-based gas sensor by using Multivalent Amino-Functionalized Calix [4] arenes, which can achieve self-assembly and absorption [8]. You-Ting Wu *et al* have studied the frequency response of QCRs with different electrodes (silver or gold), roughness and proposed a new calculation formula considering the roughness [9]. Basically, the sensitivity of QCR-based gas sensor is dependent on its gas molecule adsorbing capabilities. QCR will have resonant frequency shift due to a mass change induced by adsorbed gas molecules. The adsorption depends mainly on the physical process, where the adsorption is reversible and gas molecules can be easily released from the sensor. Associated with other gas-sensitive materials and structures, QCR-based gas sensor can be applied to different gas species. However, the physical adsorption process for QCR-based gas sensor still remains unclarified, and it is still a question that how does QCR-based gas sensor respond to different gas concentration.

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This paper proposes an innovative gas-solid physical adsorption model, where sensitivity of the resonator is dependent on the adsorbed gas molecules. The proposed modeling is established on Langmuir Adsorption Theorem [10] and Sauerbrey Equation [11]. The relationship between CO_2 concentration and frequency shift is firstly derived and lab experiment is then carried out to verify the modeling and retrieve the surface concentration constant and Langmuir constant, which are considered as very important material properties to evaluate its gas sensing capabilities.

2. Langmuir adsorption and frequency response of QCR

2.1. Langmuir adsorption modeling

Adsorption is one of the basic surface interaction. Different from chemical adsorption, for gas sensor application, physical adsorption is dominant, which does not have a significant change in the electronic orbital patterns of the species involved and thus is reversible. This paper proposes an innovative CO_2 gas sensing modeling based on the Langmuir adsorption theorem, which assumes that there are centain numbers of active sites on the adsorbent surface and these sites will be occupied by CO_2 molecules and then form a monolayer. [12]. Fig. 1 shows the schematic of typical Langmuir monolayer adsorption at the gas-solid interface.

The adsorbing rate is dependent on the partial pressure of CO_2, the occupied active sites of the surface, and the surface concentration at the monolayer coverage of adsorbate. The maximum occupation is determined by the given temperature [12,13]. Langmuir adsorption is a dynamic process and at equilibrium, the adsorption rate is equal to the desorption rate [12], which can be expressed by Eq. (1).

$$p\left(1-\frac{S^A}{S_m^A}\right)\exp\left(-\frac{E}{RT}\right) = k'\left(\frac{S^A}{S_m^A}\right)exp\left(-\frac{E'}{RT}\right) \tag{1}$$

where p is partial pressure of CO_2, S^A is the concentration of the occupied active sites on the surface, S_m^A is the surface concentration at the monolayer coverage of the adsorbate, which defines the maximum sites that the adsorbent can provide for gas adsorption process, $\exp(-(E/RT))$ is the activation energy of an adsorption, k' is the proportional coefficient. At room temperature, it is assumed that the heat of adsorption is not dependent upon the surface coverage, so Eq. (1) can also be expressed as,

$$k = \frac{S^A}{p(S_m^A - S^A)} \tag{2}$$

where k is the Langmuir constant depending on temperature only and indicates the number of active sites that participating into the gas adsorption process. Eq. (2) is called Langmuir adsorption isotherm [12].

2.2. Frequency response of QCR (Modified Sauerbrey Equation)

The gold electrodes of QCR have been proved to be able to adsorb CO_2 molecules [9] and form a monolayer of adsorbate at the gas-solid interface. As a result, the adsorbed CO_2 molecules are considered as Sauerbrey mass, Δm and will cause the QCR resonant frequency shift according to Sauerbrey Eq. [11],

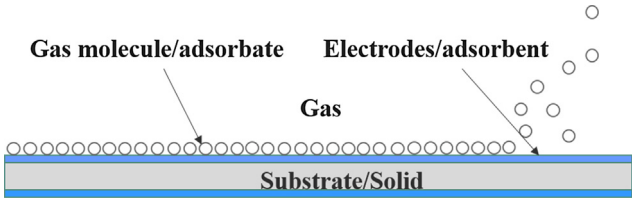

Fig. 1. Langmuir adsorption with monolayer.

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}}\frac{\Delta m}{A} = -\frac{2f_0^2}{\rho_Q v_Q}\frac{\Delta m}{A} \tag{3}$$

where f_0 is the resonant frequency, A is the active electrode area, ρ_Q is the density, μ_Q is the shear modulus and v_Q is the shear wave velocity of the quartz crystal. The Sauerbrey mass, Δmcan be rewritten in terms of Langmuir adsorption. By insertin h g Eqs. (2–4) to Eq. , the relationship between QCR frequency shift and CO_2 concentration can be described by Eq. (4),

$$\Delta f = \frac{-2f_0^2}{\pi R^2\sqrt{\rho_Q \mu_Q}}\rho_{co_2} S_m^A\left(\frac{kp}{1+kp}\right)\pi r^2 h \tag{4}$$

where R is the radius of quartz crystal, ρ_{co_2} is density of CO_2, r is radius of gold electrodes, is diameter of CO_2 molecule. According to Eq. (4), the sensitivity of the QCR to CO_2 is mainly dependent on the adsorbent and in terms of surface concentration at the monolayer coverage of adsorbate, S_m^A and Langmuir constant k, respectively.

Fig. 2 shows the isotherms of QCR at different surface concentration S_m^A, which has a significant influence on the adsorption process of the QCR as it determines the maximum adsorption capability of the material. Frequency shift is more likely to get saturated at higher CO_2 concentration when S_m^A is small. This is because the maximum sites that the material can provided for adsorption is limited. So from sensor development point of view, a large S_m^A is preferred.

Fig. 3 shows the isotherms of QCR at different Langmuir constant k, which is proportional to the temperature [12,13]. Higher Langmuir constant will ensure more active sites to participate into the adsorption process and thus higher frequency shift. However, there is also a following saturation stage for frequency shift at high CO_2 concentration due to the limit of CO_2 adsorbing capability is reached, which is determined by the term of $kp/(1 + kp)$ in Eq. (4). Therefore, from the sensor development point of view, there is a tradeoff between the choices of Langmuir constants. The QCR CO_2 gas sensor will keep a better linearity but a smaller sensitivity (slope) with a lower Langmuir constant and vise verse. So for low CO_2 concentration measurement, higher Langmuir constant is preferred for the sensor design while for a large range CO_2 concentration, a lower Langmuir constant will ensure the linearity of the gas sensor.

3. CO_2 Sensing experiment setup

Lab experiments are carried out to verify the Langmuir adsorption modeling of QCR with gold electrodes. The QCR used in the experiment is AT-cut quartz crystal with a resonant frequency of 4.89 MHz as shown in Fig. 4(a), (b) shows the dimension schematic diagram.

In order to test the QCR response to CO_2 at different concentration, N_2 is applied as reference gas. Fig. 5 shows the schematic diagram of the experiment setup. CO_2 concentration is controlled by mixing with reference gas, N_2, by a proportioner/mixer (AALBORG G gas proportioner). Then the mixed gas is flowed into a sealed, self-designed gas chamber as shown in Fig. 6. When the QCR inside the chamber is exposed to the mixed gas, the QCR resonant frequency will be maintained by the frequency counter (KEYSIGHT 53210A RF Counter 350 MHz), shown in oscilloscope (Tektronix TDS 3054C 500 MHz, 5GS/S) and recorded by the application of LabVIEW (Version 2015).

To start the experiment, the gas chamber is purged by pure nitrogen for 10 min to get rid of the remaining air. The QCR resonator is installed in the housing device and exposed to the inflow gas. The experiment begins with pure nitrogen and then CO_2 is introduced by controlling the gas composition. Concentration of CO_2 is adjusted from 0% to 100% (with a step of 25%) and kept constant for each step.

4. Results analysis and discussion

The resonant frequency of QCR with respect to CO_2 concentration change are shown in Fig. 7. LabVIEW program is applied to process and