The Effect of Humidity Levels on Carbon Dioxide Gas Concentration Measurement using a Titanium Dioxide-Coated Quartz Crystal Microbalance

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Abstract: Carbon dioxide (CO_2) is an odorless and colorless gas in ambient air. Carbon dioxide is one of the greenhouse gases that is related to climate change. Carbon dioxide gas is released by many sources and exhaled by humans and animals in ambient air. Carbon dioxide gas concentration can be measured using several techniques. However, the most important thing is the ability to measure carbon dioxide gas concentration in a high-humidity environment, such as high-cost maintenance, specific operators, sensor replacement, decreased performance, and many others. In line with this, this study aimed to develop a carbon dioxide gas sensor using a quartz crystal microbalance and TiO_2 layer. This study also identified the influence of the humid environment on the sensor's performance. The TiO_2-coated quartz crystal microbalance sensor was installed inside a box and connected to a frequency counter to measure the frequency shifts. Then, the sensor was exposed to the sample gas (concentration = 10,000 mL/m^3) with varied humidity levels: 60%, 69%, 79%, 89%, and 99%. The humidity variations were controlled using a humidity level controller. These sensor evaluations were conducted inside an experimental chamber. The results show that the low humidity levels (60% and 69%) have the fastest response times (1 s). The high humidity levels (89% and 99%) show the slowest response time (6 s). The best accuracy (75%) and sensitivity levels (0.0045 Hz/ppm) are obtained from the low humidity level (60%). It can be concluded that the TiO_2-coated quartz crystal microbalance sensor can be used as a carbon dioxide gas sensor with a humidity <80%. The humidity level influences the sensitive layer of the sensor due to the existence of water molecules. A lower humidity level, a higher sensor performance.

Keywords: carbon dioxide; humidity; quartz crystal microbalance; titanium dioxide

1. Introduction

The impact of global warming is commonly identified by the average Earth's surface temperature increase. Global warming is also related to greenhouse gases[1–3]. The biggest contributor of greenhouse gases is carbon dioxide or CO_2 gas (72%)[4,5]. The increase in CO_2 gas is found in many regions, including Indonesia, Japan, Thailand, and other countries. The increase of CO_2 gas is influenced by the increase of emission sources, such as transportation, population, and industrial sectors[6–10].

A previous study identified that CO_2 gas in the atmosphere reached 410.40 ppm[11]. The increase in CO_2 gas is related to a serious health impact when the concentration is > 500 ppm[12]. Another previous study shows a significant increase in CO_2 gas concentration (about 2 ppm per year). The increase of this gas is related to several diseases, such as oxidative stress and endothelial dysfunction. Hence, a way to overcome this problem is by conducting a monitoring or mitigation system.

CO_2 gas concentrations are measured using many technologies, such as a metal oxide gas sensor[13], micro-electro-mechanical systems (MEMS)[14], non-dispersive infrared (NDIR)[15], QCM (quartz crystal microbalance)[16], and many others. NDIR is a low-cost principle with a compact size, easy process control, continuous measurement, and high sensitivity. However, the most disadvantage of this principle is unstable measurement due to the influence of humidity and temperature changes[17]. In contrast, a QCM-based sensor has an advantage in its high sensitivity, real-time, and rapid response. A QCM also has rapid recovery times, good linearity, high stability, and good control for humidity parameters[18].

QCM Working Principle

A QCM sensor has a specific fundamental frequency (f_0) that depends on the electrode's material and crystal characteristics. QCM works due to the mass deposition on its surface with the principle of quartz crystal frequency[18)]. In other words, a QCM crystal is a mass sensor where the measured frequency decreases linearly to the mass changes[19)]. QCM-based sensors are also easy to develop due to the flexibility of surface modification using many functional layers[20)]. The surface modification is related to the QCM performance as the sensing element since a bare QCM performs as a mass detection only. For a specific analyte or targetted substance, the surface of the QCM has to be modified or coated using a sensitive material that can react with the targetted substances[21,22)]. Due to this characteristic, QCM has the potential to be developed as a gas sensor using a specific coating material.

Titanium Dioxide (TiO_2) as a Sensitive Layer

One of the most popular QCM coating materials or layers is titanium dioxide (TiO_2). TiO_2 has good chemical stability and low toxicity. TiO_2 is relatively considered a low-cost material with a unique characteristic[23)]. TiO_2 is easy to be modified for a sensor development with a good electronic and optic characteristics[24,25)]. The TiO_2 layer has been used as a CO_2 sensor with varied performances. However, recent studies have yet to identify the humidity or moisture content effect on the sensor's performance, since humidity level is important in atmospheric gas measurement[17)]. Moreover, a good sensor that performs well in a humid environment is also important. In line with this, this study aims to develop a CO_2 gas sensor using a titanium dioxide layer. This study also identifies the influence of humidity on the sensor's performances, including accuracy, sensitivity, linearity, and response time.

2. Materials and Methods

2.1. Sensor Preparation

This study used QCMs (base frequency f_0 = 4.995 MHz, silver electrodes, purchased from PT. Great Microtama Electronics Indonesia) as the bare sensors. All QCMs were coated using nano-TiO_2 layers (anatase phase, 2 molars) diluted in aquabides. The coating process was conducted using a spin coating method (5μL, 500 rotation per minute for 10 s and 2500 rotation per minute for 60 s). The coated QCMs were naturally air-dried inside a vacuum chamber and tested using a frequency counter[26,27)]. The surface of the coated QCMs were characterized using a SEM (scanning electron microscope, JEOL-JCM7000). The as-prepared sensor was installed in a sensor box (Fig. 1).

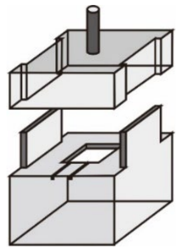

Fig. 1: The schematic design of the QCM box.

2.2. CO_2 Gas Measurement

The performances of the QCM sensors were evaluated using pure CO_2 gas (Fig. 2, purity = 99.98%, purchased from PT. Malson Gas Indonesia) inside an experimental chamber (volume V = 0.03 m^3, flow rate Q = 1 L/minute). The gas humidities were varied into five variations (60%, 69%, 79%, 89%, and 99%) using a humidifier (humidity controller) to investigate the influence of humidity level on CO_2 measurement. For the first step, the humidifier was connected to the gas tube and set to 60%. The gas sample was injected into the experimental chamber with a constant Q (1 L/minute) for 18 s. This step generated 300 ml of CO_2 gas inside the chamber (concentration = 10,000 mL/m^3). The sensor was installed inside the experimental chamber and connected to a frequency counter to measure the frequency shift (Δf). These processes were also conducted to identify the response (t_{rs}) and recovery times (t_{rc}). These treatments were conducted for all humidity variations. The humidity and temperature levels were measured using a digital sensor.

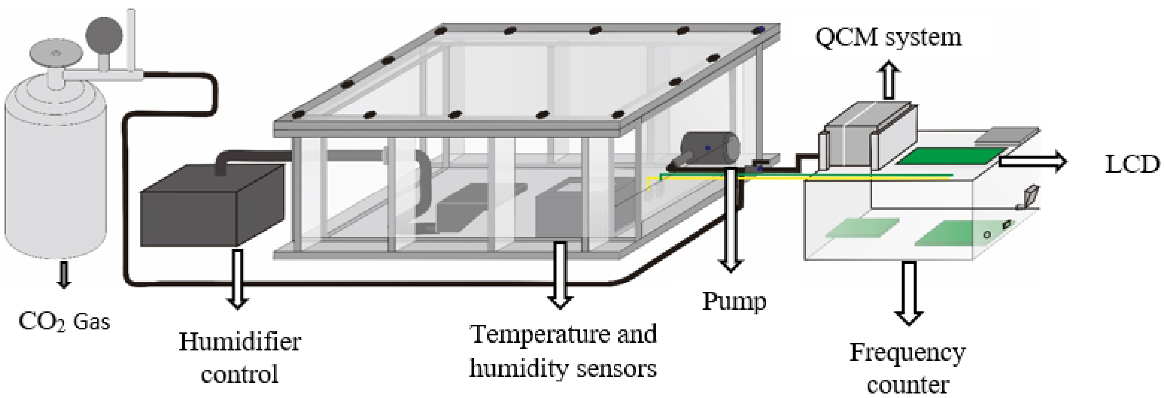

Fig. 2: Experiment setup for the performance test.

2.3. Performance Evaluation

All data were written as the mean and SD (standard deviation). The frequency shift of each sensor (Δf) was calculated from the difference between f_0 and f[28]. According to Sauerbrey's equation, a higher frequency shift interprets more deposited CO_2 gas. The deposited mass, Δm, is linear to the frequency shift (Δf) (Eq. 1). A is the area of the sensor's electrodes, while μ_q (2.947×10^{11} g/cm s^2) and ρ_q (2.648 g/cm^3) are the shear modulus and density of the quartz, respectively. The accuracy level was calculated by comparing the gas concentration (10,000 mL/m^3) and deposited gas mass (Δm). The differences in the sensor's frequency responses in measuring the gas concentrations were evaluated using a one-way ANOVA (analysis of variance) test, where $p < 0.05$ was considered statistically different.

$$\Delta m = - \frac{A\sqrt{\rho\,\mu}}{2\,f_0^2} \cdot \Delta f \qquad (1)$$

3. Results

3.1. Surface observation

Figure 3 shows the sensor's morphology with the TiO_2 layer. It can be seen that there is a rigid and uniform layer on the surface. The particle distribution is observed at ±200 nm (classified as fine particle).

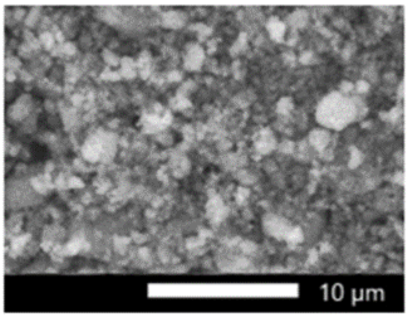

Fig. 3: Morphological images of TiO_2 on the QCM surface (Scale bar = 10 μm).

According to the measurement, the initial frequency of a bare QCM sensor is 4.995 MHz. The measured frequency of the QCM after being coated is 4.990 MHz. The frequency difference is about 5.135 kHz. This low-frequency difference indicates a low impedance due to a stable oscillation frequency, a uniform surface, and a rigid surface. In other words, the titanium dioxide was successfully coated on the QCM's surface (0.259 μm).

TiO_2 coating is a technique to increase the performance of a QCM sensor. As a requirement in developing a selective gas sensor, a QCM's surface must be analyzed, including the roughness level, particle distribution, and coating thickness[29]. A nanometer-scale particle is useful for getting a bigger volume fraction and higher porosity. As an impact, it may increase the adsorption ability[30].

3.2. Frequency and response times

Figure 4 shows the sensor's responses under different humidity levels. This figure interprets that the first humidity variation (60%) has the fastest response time. This variation has only 1 s in giving the first response under CO_2 gas concentration (Δf = -45 Hz). The second position belongs to the second humidity variation (69%), showing a response time of 1 s (Δf = -34 Hz). The third humidity variation (79%) shows the third position: 2 s (Δf = -32 Hz). Both 89% and 99% humidity levels do not interpret good response times (the response times are 6 s). These two humidity variations have low-frequency shifts (Δf < 30 Hz). The fastest response time shows the best sensor response under CO_2 gas. Then, the biggest frequency shift also indicates better gas detection using a QCM sensor ($p < 0.05$).

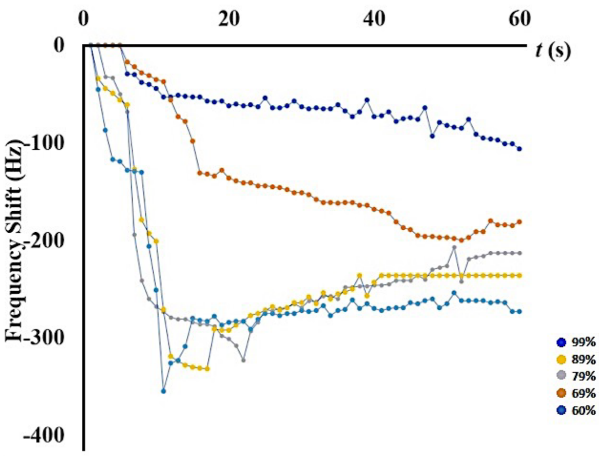

Fig. 4: Frequency responses of the QCM sensors under humidity levels

3.3. Sensitivity and accuracy levels

Figure 5 interprets the accuracy and sensitivity levels of the sensors under different humidity levels. It can be seen that the first, second, and third humidity variations have accuracy levels > 70%. These humidity levels also have good sensitivities, 0.0032-0.0045 Hz/ppm. In contrast, 89% and 99% humidity levels have low accuracy (< 70%) and sensitivity levels (< 0.0030 Hz/ppm). A higher sensitivity level indicates a better sensor response. Meanwhile, a higher accuracy level indicates a better sensing result in a measurement system.

4. Discussion

The results indicate that the QCM and TiO_2 layer can be fabricated as a CO_2 gas sensor. According to the sensitivity and accuracy levels, including the response time, it can be seen that the system performances are related to the humidity variations. Thus, the sensitive layer and the humidity levels influence the sensing parameters.

The TiO_2 layer has specific crystal phases that influence the material sensitivity regarding CO_2 or other analytes.

This characteristic can be applied as a sensitive layer for sensor development using a QCM. Generally, a QCM sensor has three working phases: active zone (frequency decreases linearly to the increasing deposited mass), steady state (maximum resonance), and recovery state (back to initial frequency). In this study, the sensor might have a maximum condition or steady state and relaxation time when exposed to CO_2 gas.

The sensing mechanism of CO_2 gas with a TiO_2 layer is related to oxygen adsorption (Fig. 6). This mechanism can be investigated in the surfaces of the QCM when exposed to CO_2 gas (both physisorption and chemisorption processes)[22]. These two reactions are related to the temperature fluctuation (as well as the humidity level) and oxygen molecules. Oxygen molecules may adsorb on the surface of the TiO_2-coated QCM sensor by the physisorption process due to Van der Waals bond. There will be several dipole interactions that can adsorb oxygen molecules. As a chain reaction, there will be new substances: chemisorbed oxygen species (O_2^-) on the QCM electrodes. Since QCM is a microbalance crystal, adding mass to its surface causes a decreasing frequency. When the maximum resonance occurs (due to the bindings of the oxygen atom from humidity and the Ti atom), it causes a stagnant response in the QCM sensor (humidity > 79%) and the sensor cannot reach the initial frequency[31,32]. In other words, the sensor optimally works at the humidity <80%.

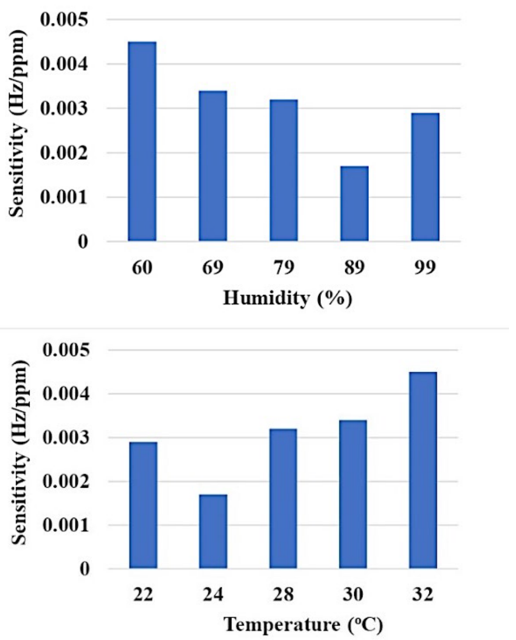

Fig. 5: Sensitivity levels: (a). humidity; and (b). temperature.

The most problem of the measurement is the issue of water molecules. Hence, more CO_2 exposure with high moisture content might cause a maximum resonance on the sensor's electrodes. When TiO_2 reacts with humid CO_2, the moisture content is observed on the sensor's surface and interacts with TiO_2. This interaction may generate a new layer (with water molecules) due to the hydroxyl group[33]. As the impacts, this interaction may decrease the flexibility and reversibility of the sensor (as found in the high humidity levels). These results indicate that the high humidity levels (80-99%) have low sensitivity and accuracy levels due to the mass-loading effect.

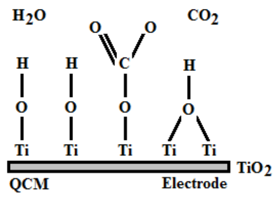

Fig. 6: Interactions between TiO_2 and CO_2 and H_2O.

5. Conclusion

In summary, a CO_2 gas sensor using a TiO_2-coated QCM is fabricated and evaluated under different humidities: 60%-99%. The humidity variations are used to identify the influence of the humid environment in the sensing performances. The sensor works well in detecting and measuring CO_2 gas concentration with humidity <80%. The fastest response time, 1 s, is obtained at the humidity level of 60-69% (accuracy >70%). The sensitivity levels are 0.0017 to 0.0045 Hz/ppm. A lower humidity has a higher sensor performance in sensing CO_2 gas.

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Nomenclature

Δm	deposited mass (μg)
t_{rs}	response time (s)
f_0	fundamental frequency (Hz)
f	frequency (Hz)
Δf	frequency shift (Hz)
Q	flow rate (m_3/s)

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