Fabrication of thin film potentiometric CO_2 sensors on differentiate substrate surfaces and their characteristics

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Two kinds of planar-type potentiometric CO_2 gas sensors using thermal evaporated Li_3PO_4 thin film as solid electrolyte were fabricated. Alumina plates with rough and smooth surfaces were used as the substrates of the sensors. X-ray diffraction analysis, atomic force microscopy and scanning electron microscopy were used to characterise the Li_3PO_4 films. The sensing properties were investigated in the range of 500–5000 ppm CO_2 concentrations at 480°C. Both the rough substrate-based sensor (r-sensor) and the smooth substrate-based sensor (s-sensor) were sensitive to CO_2 gas and showed a good Nernst behaviour. The output electromotive force (EMF) of the s-sensor showed a more stable signal than the r-senor. The ΔEMF/decade values obtained from the r-sensor and the s-sensor were 45 and 55 mV/decade, respectively. The response and recovery time were not primarily influenced by the electrolyte film. It was found that the sensitivity of the s-sensor was closer to the theoretical value. The results revealed that the substrate surface roughness may influence the characteristics of Li_3PO_4 film and the response properties of the sensors to CO_2.

1. Introduction: Since the industrial revolution, there has been a rapid increase of greenhouse gases caused by increasing use of fossil fuel. It was not until the last few decades that humans became aware of the global climate crisis from the greenhouse effect. With rapid climate change and fast deterioration of people's living environments, there has been an increasing need for the detection and control of greenhouse gases. In detecting the major greenhouse gas (CO_2 gas) which arises from many fields of industrialisation, solid state potentiometric gas sensors have been studied for years [1–7]. Among these researches, sensors with a lithium ion transporting solid electrolyte and two electrodes (a sensing electrode and a reference electrode) have been paid much attention owing to their good sensing performances [8–10].

CO_2 sensors based on bulk-type and film-type Li_3PO_4 have been reported [11–16]. The film-type sensor can be miniaturised for low-power consumption as well as low-cost applications. Response characteristics of the sensors based on Li_3PO_4 film with thicknesses of 0.3, 0.65 and 1.2 μm to CO_2 and the effect of the thickness of the electrolyte film on response property has been reported [15]. The results revealed that the ΔEMF/dec values increased with increase of electrolyte thickness. However, some work still needs to be done when making miniaturised thin film gas sensors. It is unlike bulk-type electrolytes which are thick and needless of a substrate when fabricating a gas sensor. When designing a film-type sensor, a substrate is needed as a predecessor. However, the surface roughness of the substrate may influence the characteristics of the electrolyte film. This is due to the comparable dimensions between thin film thickness (about 1 μm) and substrate roughness (about 0.1 μm to several nm). Surface roughness may also affect the response property of the sensor. The influence of roughness on the performance of the sensor based on thin electrolyte film will be a new and interesting subject, which may help us to accurately design such kinds of sensors.

To investigate the effect of substrate roughness on a film-type gas sensor, a sensor based on rough substrate (r-sensor) and a sensor based on smooth substrate (s-sensor) with thermally evaporated lithium phosphate (Li_3PO_4) thin film were fabricated. The structures of the sensors were: CO_2, O_2, Au, $Li_2CO_3|Li_3PO_4|TiO_2 + Li_2TiO_3$, Au, O_2 and CO_2. In this reported work, substrates and electrolyte films were analysed. The response properties of the sensors were investigated. The work provides a clue to improving the performance of thin film type electrolyte gas sensors in the future.

2. Experimental details: The schematic of the gas sensor and of its fabrication process are shown in Figs. 1*a* and *b*. Alumina plates with a rough surface and smooth surface were used as the substrate of the sensors. The rough surface substrates were directly made from an industrial moulding process, whereas the smooth surface substrates were subsequently polished to obtain a smaller surface roughness. The dimensions of the Al_2O_3 substrates were $10 \times 10 \times 0.5$ mm^3. The substrates were immersed in acetone and washed for 10 min by the method of ultrasonic washing. Then, they were cleaned with alcohol and deionised water and dried. Li_3PO_4 (Aldrich, 99.99%) powder was used as the electrolyte and it was deposited on the two kinds of substrates by the thermal evaporation method with a working voltage of 4.2 V, current 180 A and working pressure of 3×10^{-3} Pa. The thickness of the films on the rough substrate and smooth substrate was measured to be about 1.0 μm. The as-deposited thin films were sintered at 700°C for 2 h in a tubular furnace in the air atmosphere. Two Au electrodes were sputtered on the electrolyte films to have a fine contact with the electrolyte film and the thickness was about 400 nm. The reference electrode materials were composed of Li_2TiO_3 (Aldrich, 99.99%) and 10 mol% TiO_2 (Shanghai Chemical Reagent Research Institute, 99.99%). The reference materials were mixed with an organic vehicle consisting of alpha-terpineol and ethyl cellulose. Then, the paste was screen printed on the Au electrode and sintered at 700°C for 1 h. The thickness of the reference electrode was about 15 μm. In a similar way, a Li_2CO_3 (Sinopharm Chemical Reagent Company Limited, 99.99%) sensing electrode with thickness of 10 μm was prepared and sintered at 600°C for 1 h. Finally, Pt wires were attached on the gold electrodes and annealed at 600°C for 2 h to make good contact.

An X-ray diffractometer, atomic force microscope (AFM) and scanning electron microscope (SEM) were used to characterise the Li_3PO_4 thin films based on rough and smooth substrates.

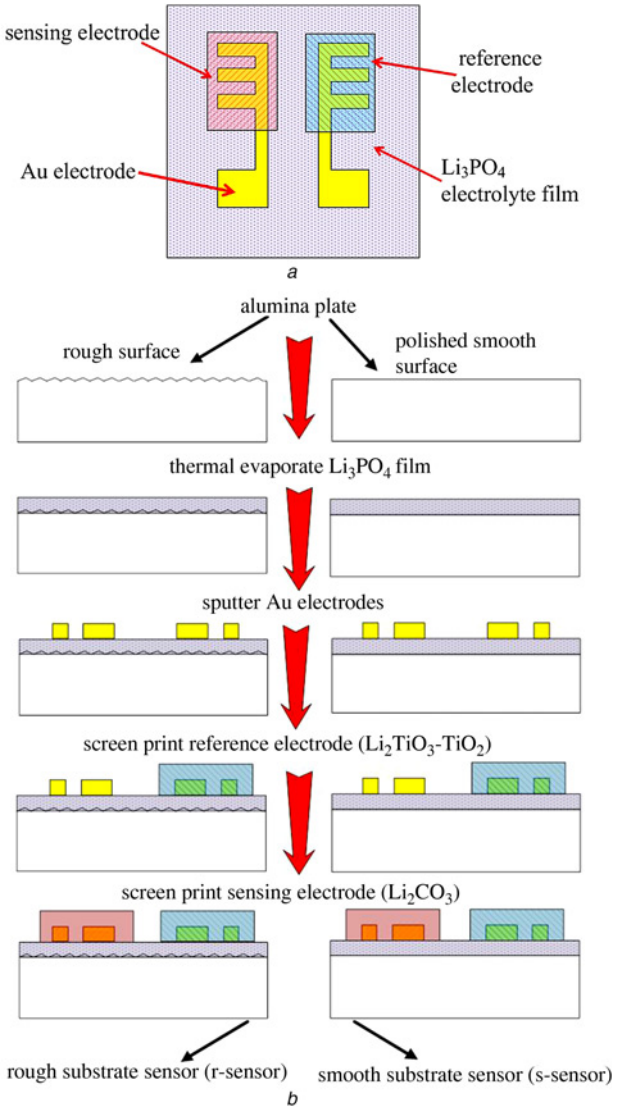

Figure 1 *Schematic of gas sensor, and of fabrication process*
a Gas sensor
b Fabrication process

3. Results and discussion: X-ray diffraction (XRD) patterns are shown in Fig. 2. Li_3PO_4 material was confirmed in the two kinds of films and the results revealed that the annealed Li_3PO_4 films were the γ-phase. The peaks of Li_3PO_4 are marked with symbol ■. However, when comparing the diffraction pattern of the smooth substrate-based film (*b*) with the rough one's (*a*), some peaks [(141), (311), (042), (160)] of Li_3PO_4 between 40° and 55° have not been found. The crystal orientations were influenced by the substrates. It means that the recrystallised electrolyte film on the smooth substrate had much more centralised crystal orientations which may be preferable for a simple film structure.

To study the influence on electrolyte films by differentiate substrate, three-dimensional (3D) morphologies of the substrates and electrolyte films were analysed with an AFM and NanoScope Analysis software. Fig. 3 shows the scanned images of the substrates and the Li_3PO_4 thin films on the substrates. Images Figs. 3*a* and *d* are the 3D morphologies of the rough alumina substrate and smooth alumina substrate. Average roughness values of the substrates were calculated to be 80 and 5 nm, respectively. The images of Figs. 3*b* and *e* show the 3D morphologies of the thermal evaporated Li_3PO_4 thin films before annealing, and the roughness values were 87 and 30 nm, respectively. This indicates

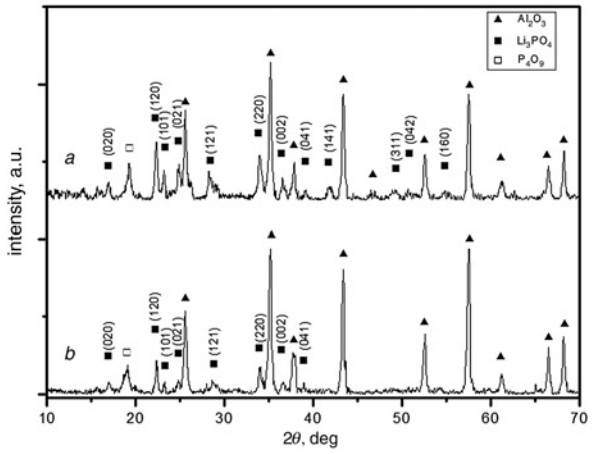

Figure 2 *XRD patterns of annealed Li_3PO_4 electrolyte films*
a Li_3PO_4 film on rough substrate
b Li_3PO_4 film on smooth substrate

that the morphologies of the deposited thin films were reflected from the substrates. It means that the smoother the substrate surface, the smaller film roughness will be. However, after annealing, the film morphologies on both the rough substrate and the smooth substrate changed a bit. As shown in the images of Figs. 3*c* and *f*, the average roughness values of the two films were 75 and 50 nm, respectively. The variations of the roughness of the films were because of the recrystallisation process of the electrolyte and there was a trend for the surface morphologies of the films to become similar. The reason may be that considerable dimensions of the peaks and valleys of the rough surface were induced randomly alongside growing paths for the evaporated thin film grains. Thus, the two films presented a difference in their morphologies. The results indicate that the surface morphologies of electrolyte thin films were influenced by both the roughness of the substrates and the recrystallisation process of the electrolyte.

Fig. 4 shows the SEM images of the annealed electrolyte films on the two substrates. Grain sizes of the rough and smooth substrates-based films were about 1–2 µm. However, the average grain size of the smooth ones was bigger. The two electrolyte films presented an obvious difference in their morphologies and grain structures. The rough one (image of Fig. 4*a*) showed a clubbed shape with a porous structure, whereas the smooth one (image of Fig. 4*b*) obtained a polygonal shape with a much denser structure. The difference of the grain structure may influence the connectivity and ion conductivity of the solid electrolyte film. The smooth substrate-based film with the compact microstructure may be a good ion conductor.

For measurement of the properties of the sensors based on two kinds of electrolyte films, different concentrations of CO_2 gases (500–5000 ppm) were synthesised via a gas distribution system. In the system, two mass flow controllers connected to a computer were used to prepare a series of different concentrations of CO_2 gas. The total flow rate of the gas was set as 200 sccm. The working temperature of the sensors was controlled by a tubular furnace (HTL1000–80). The sensing characteristics of the sensors to CO_2 were investigated at a temperature of 480°C, since at around such temperature this kind of sensor showed good properties [12, 16]. The electromotive force (EMF) was collected by a multimeter (Agilent 34410A).

For the potentiometric gas sensor, the sensing mechanism is based on the electrochemical equilibrium equations in the sensing electrode and the reference electrode. Redox reactions in the two electrodes are denoted by the following equations

$$Li_2CO_3 \Leftrightarrow 2Li^+ + 2e^- + CO_2 + \frac{1}{2}O_2 \quad (1)$$

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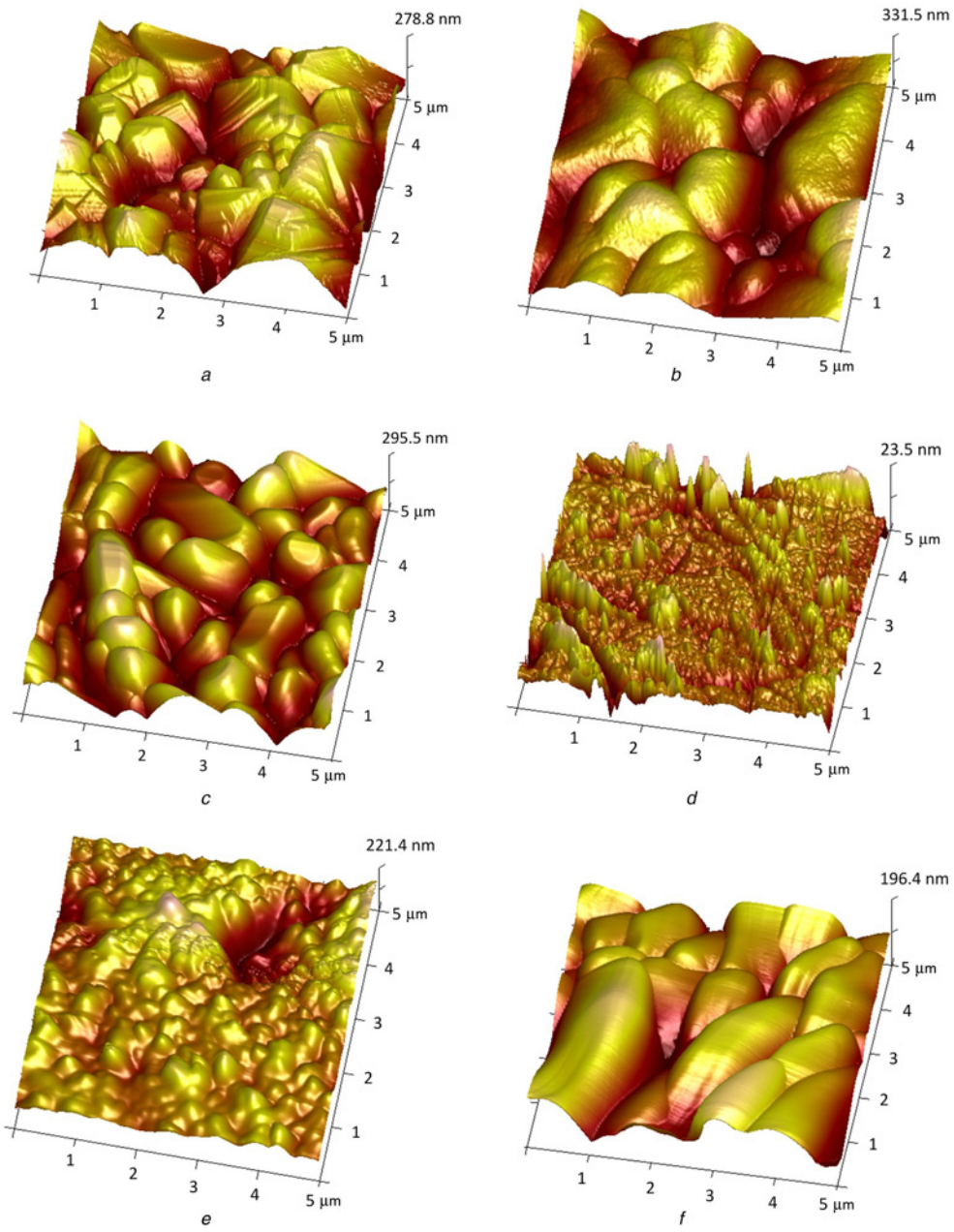

Figure 3 *AFM images*
a Rough substrate
b Li_3PO_4 film on rough substrate
c Li_3PO_4 film annealed at 700°C on rough substrate
d Smooth substrate
e Li_3PO_4 film on smooth substrate
f Li_3PO_4 film annealed at 700°C on smooth substrate

$$2Li^+ + 2e^- + TiO_2 + \frac{1}{2}O_2 \Leftrightarrow Li_2TiO_3 \quad (2)$$

and the overall reaction can be expressed by the following equation

$$Li_2CO_3 + TiO_2 \Leftrightarrow Li_2TiO_3 + CO_2 \quad (3)$$

The EMF (E) value between the two electrodes is determined by the Nernst equation in the following equation

$$E = E^0 + \frac{RT}{nF}\ln p(CO_2) \quad (4)$$

where E^0 is a certain value in a given working environment for a certain kind of sensor, R is the universal gas constant, T is the ambient temperature, n is the number of reaction electrons and F is the Faraday constant. When the temperature is fixed, the EMF value is mainly determined by the partial pressure of CO_2 ($p(CO_2)$).

Fig. 5*a* shows the output EMF of the r-sensor and the s-sensor from 500 to 5000 ppm and then back to 500 ppm at a temperature of 480°C. The sensors were tested for weeks and they obtained good reproducibility before the study was carried out. The results indicate that the s-sensor and the r-sensor were sensitive to CO_2. The EMF values decreased with increase of the partial pressure of CO_2. The r-sensor showed unstable signals throughout the whole curve, whereas the s-sensor showed a more flat signal in

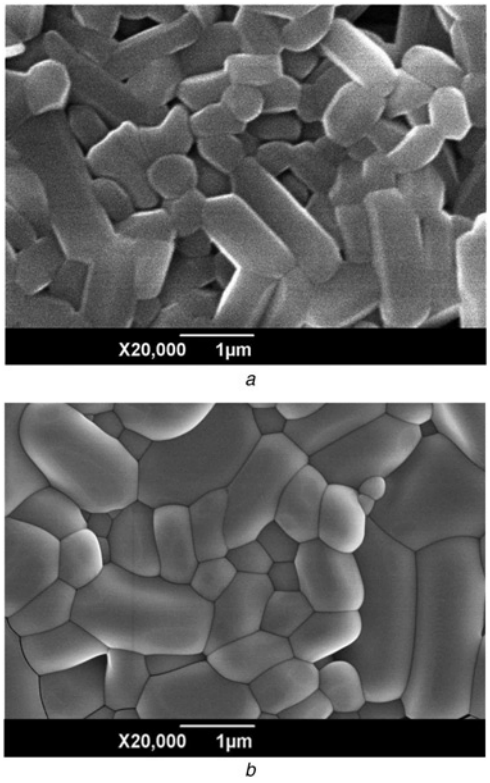

Figure 4 *SEM images*
a Li_3PO_4 film annealed at 700°C on rough substrate
b Li_3PO_4 film annealed at 700°C on smooth substrate

the testing points. The stable signals from the s-sensor may provide easy post-processing of signals when the sensor is used for applications. The absolute EMF values were increased with decrease of the surface roughness of the substrate. Fig. 5*b* is the response and recovery characteristics of the sensors from 500 to 2000 ppm CO_2 concentration. For the sensors tested, 90% average response time and recovery time were about 40 and 70 s, respectively. There was no big difference in the response and recovery time between the two kinds of sensors, although the r-sensor showed unstable signals. This means that response and recovery speed were not primarily influenced by the electrolyte film.

Fig. 6 shows that the EMF values of the sensors correspond well with the Nernst's slope in the logarithm view. The coefficients of determination of the two fitted lines were calculated to be 99.7 and 99.8%. This means that the measured values of EMF have a good linear relationship with logarithmic gas concentrations. The ΔEMF/dec values (sensitivities) of the s-sensor and the r-sensor were 55 and 45 mV/dec, respectively. The limits of detection (LOD) were calculated to be 0.029 and 0.015, respectively. It can be found that the s-sensor obtained a larger ΔEMF/dec value than the r-sensor. The ΔEMF/dec value of the s-sensor was closer to the theoretical value (74.7 mV/dec) at a temperature of 480°C. The smaller LOD value of the s-sensor was an evaluation for its stable signals. The phenomenon obtained by the experiments revealed that the ΔEMF/dec values of the sensors may be influenced by the morphologies of the electrolyte films which were reflected from the substrate surfaces. The exact mechanism of the influence has not been clearly explained so far, and in our opinion it may be attributed to ionic conductivity, different polarisation ability and other factors.

4. Conclusions: Experimental results concerning the influence of the substrate surface roughness on planar-type CO_2 gas sensors have been described in this Letter. AFM and XRD analysis

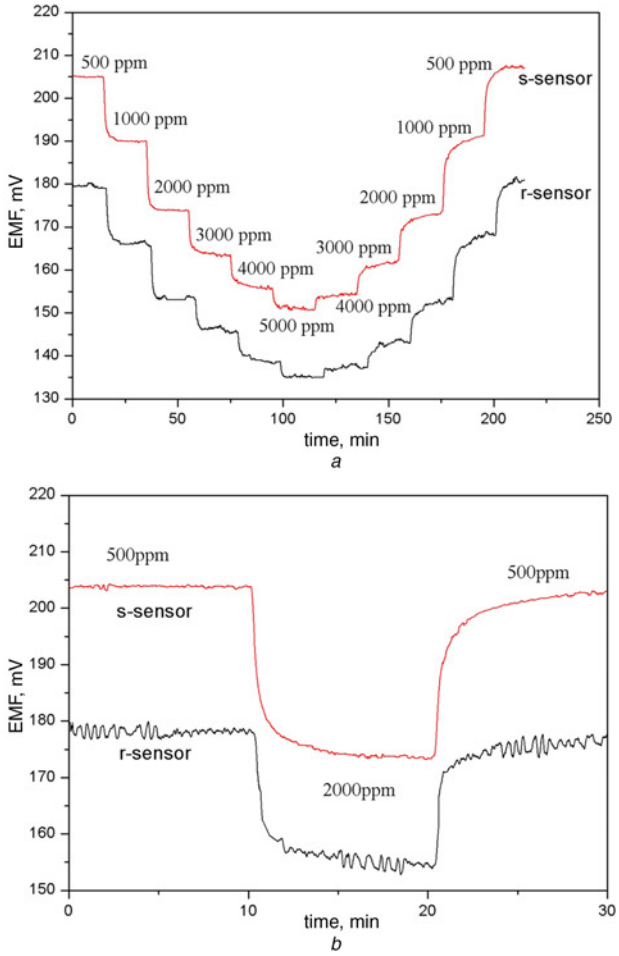

Figure 5 *EMF changes of sensors to various CO_2 concentrations (500–5000 ppm), and response-recovery characteristics of sensors from 500 to 2000 ppm CO_2 concentration*
a EMF changes
b Response-recovery characteristics

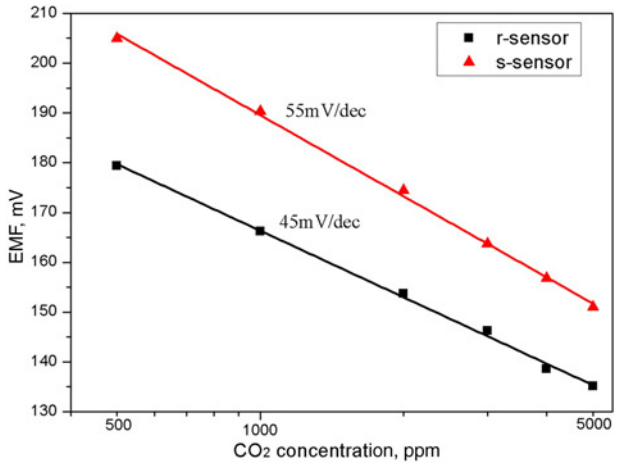

Figure 6 *EMF against logarithmic CO_2 concentrations*

showed that annealed electrolyte films were influenced by the differentiate substrate surface and the recrystallisation process of the electrolyte. The smooth substrate surface resulted in a smooth electrolyte surface. The results were confirmed by the SEM images. Analysis showed that the morphologies and crystal structures of thin films were affected by varied surface roughness

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of substrates and the characteristics of the sensors were influenced. The stability of the signals and the sensitivity of the film-type sensor were decreased with increase of substrate surface roughness. The porous morphology and scattered crystal orientations of the rough substrate-based sensor were discussed and are thought to be the reasons for these phenomena. The influence of substrate roughness on thin film electrolyte CO_2 sensors may be a reference for other thin film gas sensors.

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