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Quartz Crystal Microbalance Coated with Sol-gel-derived Thin Films as Gas Sensor for NO Detection

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Abstract: This paper presents the possibilities and properties of Indium tin oxide (ITO)-covered quartz crystal as a NO_x toxic gas-sensor. The starting sol-gel solution was prepared by mixing indium chloride dissolved in acetylacetone and tin chloride dissolved in ethanol (0-20% by weight). The ITO thin films were deposited on the gold electrodes of quartz crystal by spin-coating technique and subsequently followed a standard photolithography to pattern the derived films to ensure all sensors with the same sensing areas. All heat treatment processes were controlled below 500°C in order to avoid the piezoelectric characteristics degradation of quartz crystal (Quartz will lose its piezoelectricity at ~573°C due to the phase change from α to β). The electrical and structural properties of ITO thin films were characterized with Hall analysis system, TG/DTA, XRD, XPS, SEM and etc. The gas sensor had featured with ITO thin films of ~100nm as the receptor to sense the toxic gas NO and quartz crystal with frequency of 10MHz as the transducer to transfer the surface reactions (mass loading, etc) into the frequency shift. A homemade setup had been employed to measure the sensor response under the static mode. The experimental results had indicated that the ITO-coated QCM had a good sensitivity for NO gas, ~12Hz/100ppm within 5mins. These results prove that the ITO-covered quartz crystals are usable as a gas sensor and as an analytical device.

Keywords: Quartz Crystal Microbalance, Indium tin oxide, gas sensor, resonant frequency

Introduction

There is an increasing public concern about the presence of environmental pollutants, like nitrous gases (NO, NO_2). Thus, a requirement for the cheap and reliable sensors is urgent. It is known that quartz crystal is highly sensitive to mass changes ~1ng/cm^2. Quartz crystal-based sensors are generally fabricated by coating the surface of quartz crystal with functional thin films, which have certain reactivity to the object gas. The functional thin films include both inorganic thin films and organic thin films. Several coated crystals dedicated to the detection of single pollutants have been reported [1-3].

The reproducibility of current organic film-coated quartz crystals with a general coating method is sometimes questionable because it is difficult to regenerate the same conditions of the thin film, even through some methods like LB(Langmuir–Blodgett) film technology had been developed to fabricate thin film on the surface of quartz crystal. In addition, the high-damping polymer films will cause more power consumption and lower the sensor performance (sensitivity and response). Some inorganic thin films show very stable properties and good performance and had proven the good candidate for the functional coating. For instance, a combination of these films and the quartz crystal is expected to get a good sensitivity and stability by the properties of carbon and quartz oscillator. Indium doped Tin oxide (ITO) is well known as semiconductor oxide for resistance-type gas sensor. ITO is easily stabilized at a high temperature and very elastic in a normal environmental condition. The exploration of sol-gel techniques is due to the advantages of sol-gel processing with respect to other routes, including the low processing temperatures, the possibility of chemically tailoring the starting solutions, resulting in new compositions and in better control of the final microstructure, and the easy deposition of thin films [1,4-8]. A combination of ITO and the quartz crystal is expected to get a good sensitivity and stability. And it is easy to construct a stable sensor for application in some harsh environment.

The purpose of the work was to prepare a gas sensor by means of the widely used sol-gel technology and to investigate the sensor behavior covered with a semiconductor metallic oxide layer, ITO. First, the films were deposited by the spin-coating technique and the electrical and material properties are characterized with various techniques. Next, the study with the ITO-coated QCM as gas sensor was carried out. We hope that all these features become keystones for an accurate knowledge of the gas sensing mechanisms.

Experimental

Sol-gel ITO thin films preparation

Anhydrous indium trichloride ($InCl_3$) was dissolved in acetylacetone and the solution was refluxed at 60°C. Hydrous Tin IV chloride ($SnCl_4$) was dissolved in ethanol and this solution was mixed with the refluxed solution at room temperature to obtain the sol-gel solutions, just as reported in Ref [4]. The solution was placed on the room temperature for two days. Circular-shaped quartz crystals (with diameter of 10mm and thickness of ~167μm) were used as the substrates. The crystals of QCM were

washed with acetone, IPA and subsequently, with DI water and dried with N_2. And the films were coated by the spin coater with rotation speed of 5000rpm and time of 30s. Each time, 7μl sol-gel solution was applied though Micropippete. The coated substrates were heated at 150℃ for 10 min after each spin coating. By repeating the above procedure, indium tin oxide films with various thickness were obtained. After coating, a final annealing is proceeded with different time intervals under different temperature, including 250℃, 300℃, 350℃, 400℃, 425℃, 450℃, 475℃ and 500℃. In addition, 200μl sol-gel solution was dried at room temperature for 24hours. The residual solid material was used for the thermal analysis. The films were also deposited on the glass slide for microscopy (76×26×1.5mm) simultaneously for the measurement.

ITO thin films characterization

Thermal analysis was conducted in N_2 on a TA-Inst 2000 thermal analyzer by a heating rate of 20℃/min from room temperature to 600℃. Crystal structures were analyzed by using an X-ray diffractometer Philips X'Pert, XRD system, Cu target. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a VG-Scientific ESCA-LAB analyzer using a Mg Kα 1253.6 eV X-ray source. All measurement conditions and parameters were verified to get the right carbon peak position. The electrical properties were determined with the Van der Paul method on a Biorad Hall Effect Measurement System.

Sensor configuration

The gas sensor with ITO as the receptor is formed as below. 10 MHz 14mm diameter un-mounted polished AT-cut quartz crystals with 5.1mm gold electrodes (International Crystal Manufacturing, Oklahoma City, OK, USA). The electrodes were composed of a 50A Cr underlayer surface and a top 1000A Au layer. The calculated mass sensitivity is ~0.226ng/Hz·cm^2. The quartz crystals were detached from the trays and cycled the process as below: The quartz with gold electrodes was cleaned carefully with the acetone, IPA and DI water. Sol-gel process then was proceeded. After finishing the sol-gel process, the ITO thin films were patterned with the standard photolithography techniques and 5% HBr solution was used as the etchant for ITO etching. Thus, the resulted sensors will be with the same area of ITO coating. The coated quartz wafers were mounted on the trays and used as the sensors for gas detection. The frequency shift due to the ITO coating is controlled below 60kHz.

Apparatus for gas sensing

Gas sensing experiments were conducted using an in-house assembled gas sensing system just as Ref [3]. The apparatus consists of a sealed stainless steel chamber connected by valves A and B to the carrier (or flushing) gas source and a rotary pump respectively. Each sample to be tested was placed on the stage that can be heated to the desired testing temperature while its frequency was measured at fixed intervals by a computer program. A syringe calibrated in millimeters was used to inject the test or trace gas into the chamber (syringe with minimum calibration of 0.1ml). The output frequency was continually monitored by a TF830 universal counter (Thurlby-Thandar, UK) and finally transferred to

a computer using the RS 232C interface. The Labview ™ program was used for all measurements, data storage and processing. All processes were undertaken under room temperature (23±0.5°C). A Network Analyzer, S&A 250B (Saunders & Association Corp., USA), was also connected to the testing head.

Results and discussion

ITO thin films characterization

Differential Scanning Calorimetry and Thermal Gravimetric Analysis (DTA-TGA)

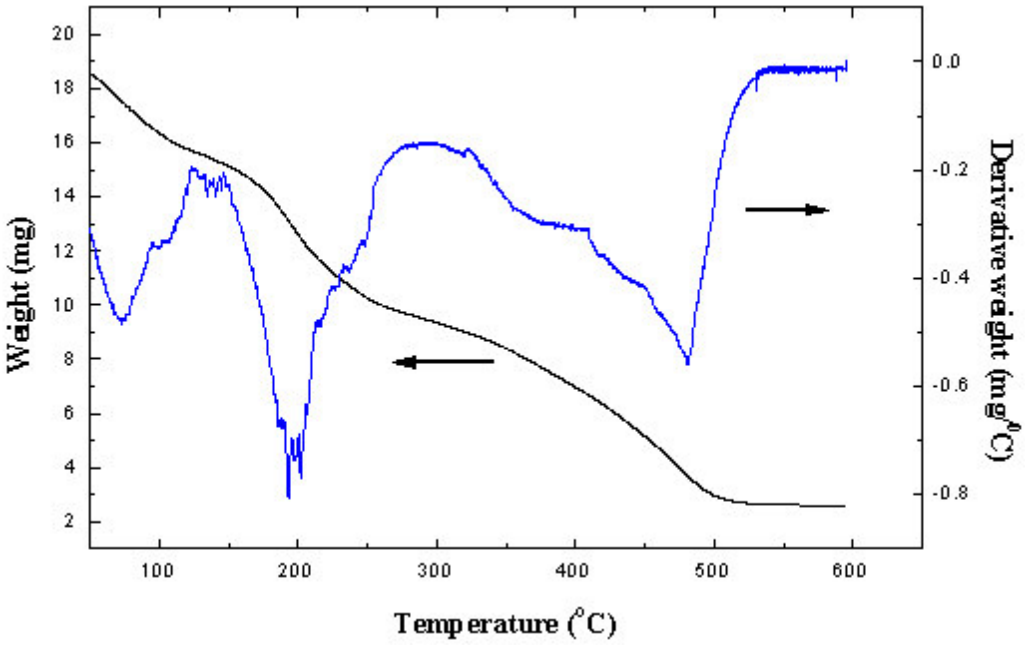


Figure 1. Thermal analysis result of evaporated sol-gel solution

Figure 1 shows the DTA-TGA curves of the corresponding ITO sol processing in N_2. Initially, an endothermic region, characterized by several peaks, is observed at temperature <200°C. These endothermic phenomena and the corresponding large mass loss, evidenced by the TG curve, can be attributed to desorption of solvents and the elimination of chloride from the powder.

Another endothermic peak is observed at 250°C and is attributed to the pyrolysis of the organic residuals in the powders. The peak is accompanied by further mass loss, evidenced by the TG curve. The elimination of the organic residuals through oxidation also is included in this region.

Finally, another exothermic peak at ~500°C is attributed to the formation of crystallization of In:SnO_2. From the figure we also note that after 500°C till 600°C, no further remarkable mass loss was found, indicating that all organic or inorganic residuals had been eliminated totally.

XRD analysis

Samples with different annealing temperatures show different behavior. Overall, heating at 150°C results in a predominantly amorphous structure. Just as previous publications, for higher heating temperatures, the diffraction peaks become progressively more intense and sharp.

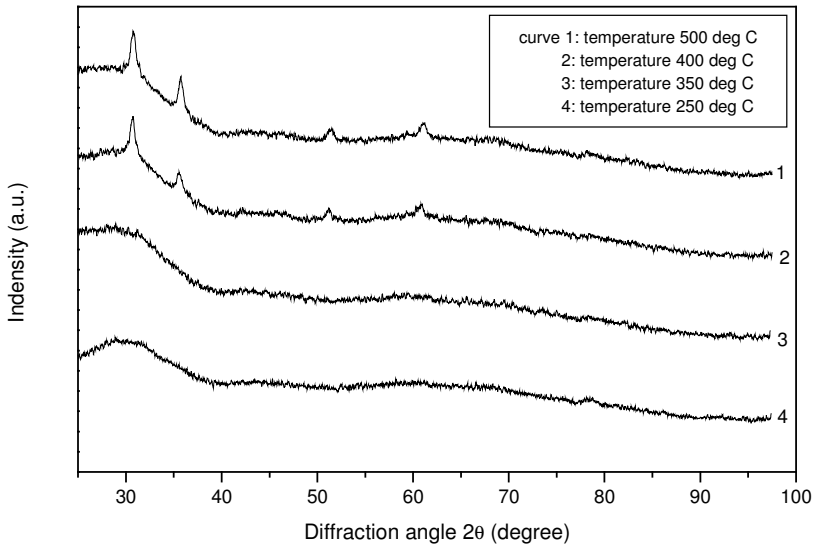


Figure 2. XRD results of samples prepared by different annealing time intervals (t=10min and t=45min)

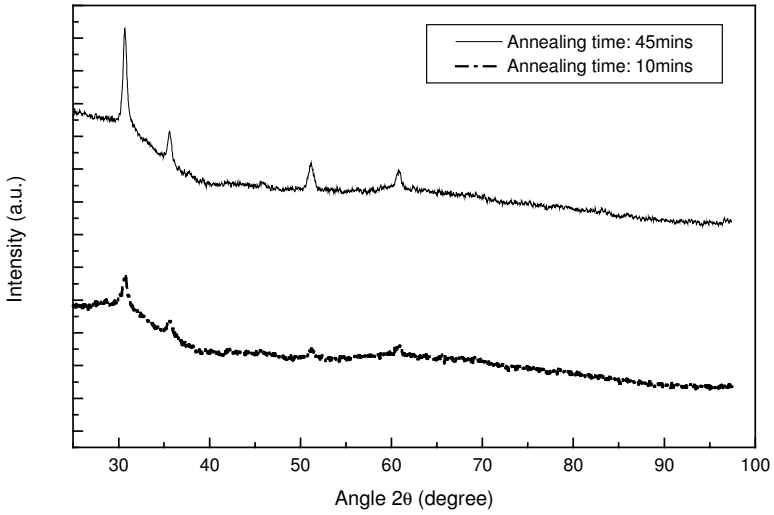


Figure 3. XRD results of samples prepared by different annealing temperature

Figure 2 showed the XRD result of sample annealed under different temperature with the same annealing time t=10min. It is noted that for T<400°C, no remarkable diffraction peaks were found, indicating the crystallographic orientation was very weak. This results is also confirmed by the TGA result showed above, indicating there exists a big endothermic process between 400-500°C. This can be understood that the high temperature is benefit to remove the organic or inorganic residual and lead to the better films structure. So the optimal annealing temperature should be > 400°C.

Figure 3 showed the XRD result of sample annealed under the same temperature but with different annealing time. It can be found that the longer annealing time can enhance the cystallographic direction. All these spectra showed that the gel films annealed at 400°C are polycrystalline with a cubic bixbyite structure with no preferred orientation. No phases corresponding to tin or to other tin compounds were detected showing that the Sn was in solution.

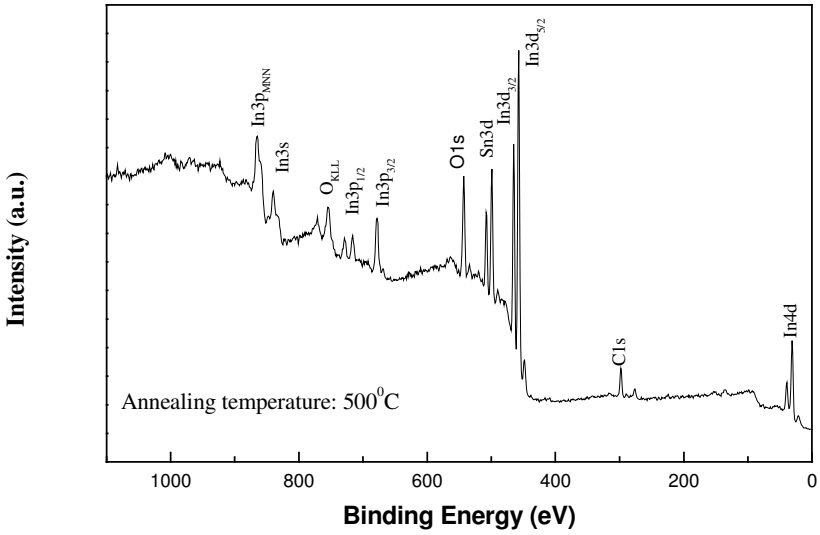


Figure 4. XPS result of the obtained sample annealed at 500°C for 45min

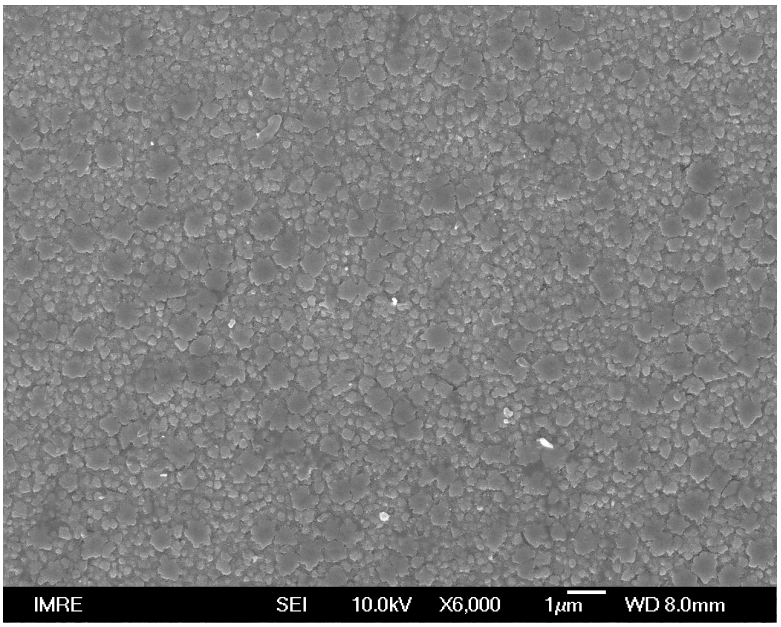
XPS analysis

X-Ray photoelectron spectroscopy (XPS) of indium tin oxide thin films with 10% tin content deposited on quartz (glass) is shown in Figure 4. Photoelectron peaks for elements In, Sn, O and C were recorded for the ITO film in the binding energy from 0 to 1100 eV. The binding energy of the O 1s photoelectron peak is at 539 eV. The C 1s peak, related to the surface pollution, at a binding energy of 285 eV is also observed on the surface of the film[4]. This peak is also connected to the organic residuals in the sol-gel solution. These show the evidence of only one binding state for In and Sn since there is no sign of broadening or splitting of the peaks. This figure is well supported by the results from Ref [4], where the sol-gel films were deposited on the glass substrates, indicating that the sol-gel deposition has nothing to do with the substrate kinds. There is no novel difference existing between the samples deposited on gold electrode and on bare glass substrates.

SEM analysis

Figure 5(a)(b) showed the SEM photo of sol-gel ITO thin film after annealing at 300℃, 475℃ for 45mins, respectively. It can be observed that no cracking was observed. In addition, it is noted that the higher annealing temperature will lead to a fine particle size. The grain size derived at 475℃ is below 100nm.

A



B

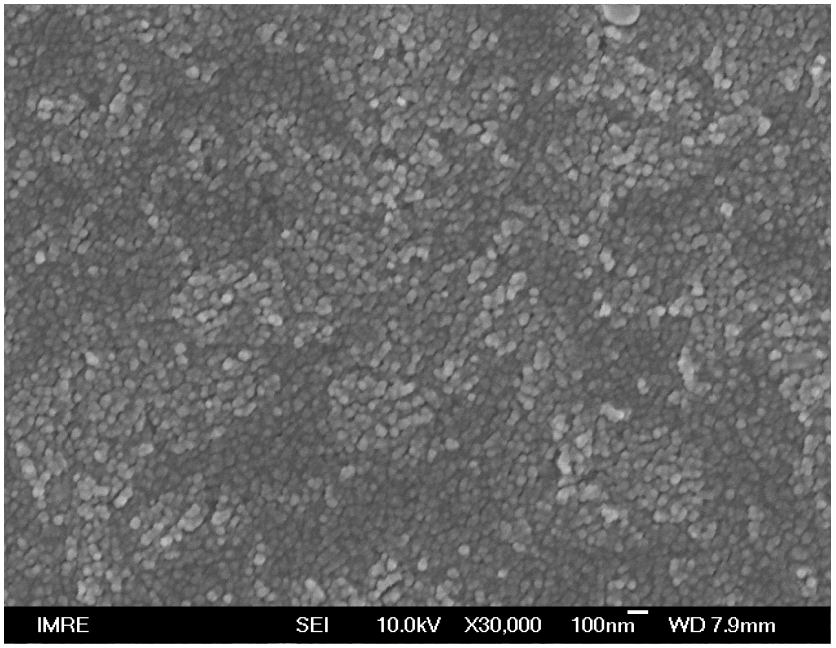


Figure 5(A). Surface SEM photo of sample prepared under 300℃ with annealing time of 45mins; (B) sample prepared under 475℃ with annealing time of 45mins.

Electrical properties

Figure 6 showed the effect of annealing temperature and time interval on the sheet resistance of 10 wt % Sn-doped ITO films annealed in air. The films were obtained only with one-time spin-coating and the resulted thin films ranged from 40nm to 80nm. Here, the variations caused by the differences of the thickness are ignored. Samples were annealed 10min (curve 1), 45min(curve2) at corresponding temperatures, respectively. The sheet resistance decreased significantly with annealing temperature up to 500°C in air. The short annealing time lead to the very high resistance, indicating that there still exist some organic solvent and other residual in the films. When the annealing temperature access to 500°C, even with the short annealing time, we can get very low sheet resistance.

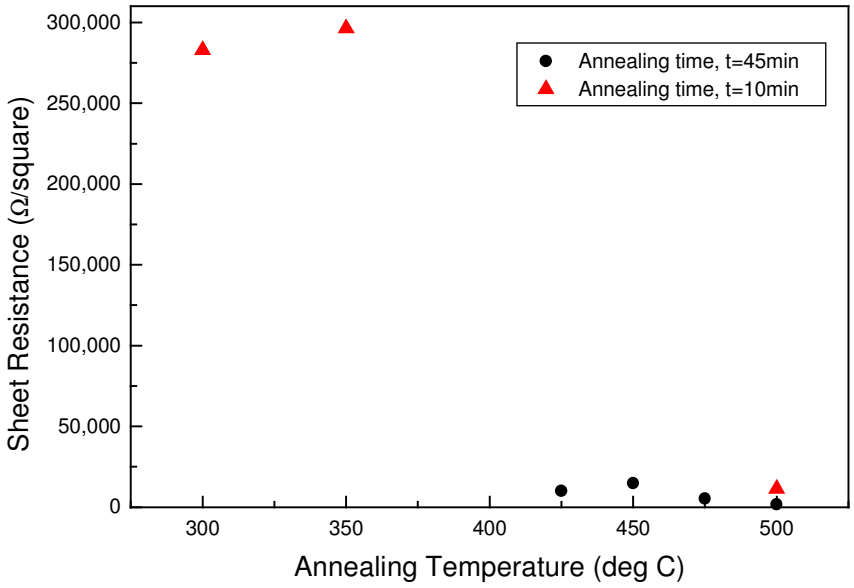


Figure 6. Sheet resistance of obtained samples (with spin-coating 1 times, annealing time of 10min and 45min respectively)

Gas sensing application

About the gas sensing, the acceptable mechanism for quartz crystal is still unclear. It is believed that the frequency shift is due to both the adsorbed gas molecules and the electrical variations due to this gas introduction.

The stability of ITO coated QCM

The electrical equivalent parameters of samples prepared under different annealing temperature can be monitored through network analyzer. Before coating, all samples show very good frequency stability (~±1Hz) with motional resistance values ranging from 7 to 10Ω [9]. After coating and different temperature annealing, the resonance frequency decreased and the motional resistance Figure 7.

Stability of the samples prepared with different annealing temperatures (all sample with the same annealing time interval of t=10min).

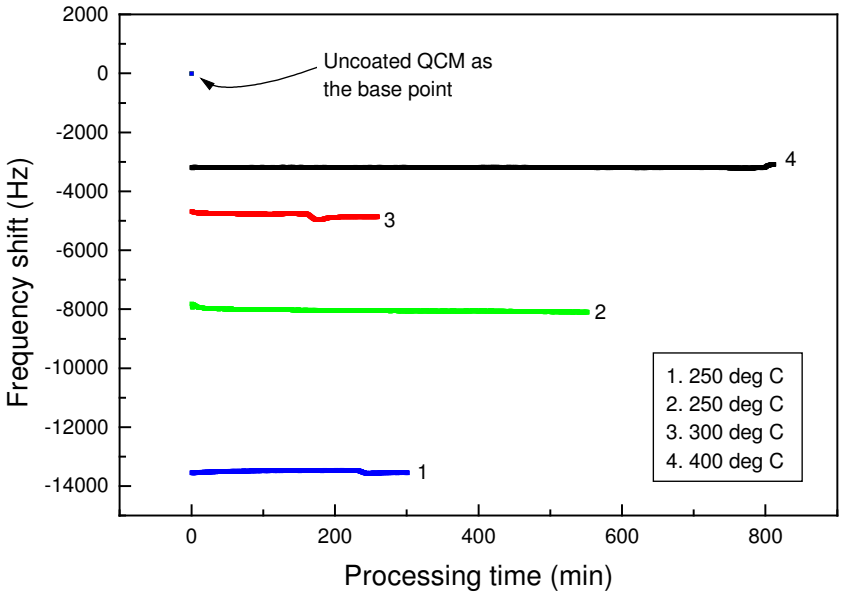


Figure 7. Stability of the samples prepared with different annealing temperatures (all sample with the same annealing time interval of t=10min).

increased. Since the higher motional resistance is also the standard to evaluate the damping effect, it is indicated that the higher temperatures result in more stable and rigid ITO thin films.

In frequency stability testing, QCMs with original frequency of 10MHz was used. The sol-gel solutions was applied and followed the annealing process. Before the stability testing, the coated QCM sensors were placed into the oven with temperature of 85°C for more than 4hours in order to remove the solvent as much as possible. Figure 7 showed the frequency response of ITO coated QCM working in air at room temperature prepared under different annealing temperature, 250°C, 300°C, and 400°C. First, we find that the sample after 400°C annealing is almost transparent. And the sample after 250°C treatment is in dark color, showing some carbon still existing in the ITO films. Second, we can find that the high temperature annealed sample indicate the smallest frequency shift, corresponding to the lowest mass loading. The low temperature annealing will show bigger frequency shift, indicating some residuals still exists in the films. Third, although thin films prepared under different temperatures, all of them showed relatively good stability in the room temperature in air, ~200Hz within 300mins. The reason for the frequency fluctuation is quite complex. It is probably due to the outgasing from ITO thin films, especially for low temperature treated samples. On the other hand, since ITO is a very sensitive material, it is believed that it can absorbed the other gases, or particles in the lab environment and result in the frequency shift. For example, we had observed the frequency change due to different humidity environment for the ITO coated QCM.

Gas sensitivity of NO gas

Just we had reported previously[3], the frequency of a freshly coated crystal upon expose to NO was found to decrease with time and no recovery was observe on subsequently exposed to clean air. This confirms the non-reversibility of the interaction of NO with the ITO thin films.

In non-reversible reaction, the frequency of the resonator changes continuously as long as the sensor is in contact with the trace gas. The relationship between the frequency shift and the gas concentration can be found elsewhere [9]. In the non-reversible interreaction, the reaction does not proceed to the equilibrium. Thus, a rate-dependent quantity expressed in Hz/min/ppm more appropriate to describe the detector behavior.

The sensors were firstly placed in the sealed chamber and the gas No was introduced just as reported in Ref [3]. It is found that as the exposure time was increased, a large amount of gas would reach the detector surface and more NO was adsorbed onto the ITO coating, resulting in a larger frequency shift. Satisfactory results were obtained after 5mins exposure. This agrees with the occurrence of a non -reversible interaction where the frequency shift is dependent on the exposure time.

When the detector was exposed to 1000ppm NO continuously for several minutes, the frequency was found to become steady, showing that saturation had occurred. Thus, the analytical performance of the resonator is governed by the total exposure time. Another useful proof is with the gas concentration increasing, the working time decrease rapidly. This is probably due to that the ITO layer is saturated and ceased to function.

Conclusion

In this paper, a detailed analysis of the noble semiconductor metal oxide ITO as obtained by sol–gel has been reported. We also presented some issues of frequency sensitivity and stability of ITO covered quartz crystal as a gas detecting sensor. The results suggest that the best temperature of heat treatment and the best film thickness of ITO are existent for getting best response of resonant frequency. The self-life and reproducibility of ITO-coated QCMs are almost perpetual and excellent because metal oxides are very stable.

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Sample Availability: Available from the authors.