Precursor and microstructure dependence of the gas and photo-detection characteristics of solution precursor plasma sprayed metal oxide coating

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Abstract

The potential of nanostructured zinc oxide (ZnO) coatings developed via solution precursor plasma spraying (SPPS) as gas and photo sensor was explored in this work. The coatings were deposited on stainless steel substrates using aqueous solutions of zinc nitrate and zinc acetate as precursors. The coatings' microstructures were influenced by the kind of precursors used. Relatively porous coatings were obtained when using acetate as compared to using the nitrate one. This was attributed to different chemical routes of ZnO formation for each precursor droplet upon contact with plasma jet. Phase analysis confirmed the formation of polycrystalline ZnO having wurtzite structure from both precursors. The fabricated ZnO coatings showed good sensitivity and recovery towards UV light. Moreover, ZnO coatings showed good response towards carbon dioxide (CO_2) analyte gas but does not show any good recovery which was attributed to the microstructure of the coatings. These results showed the feasibility of SPPS process for the fabrication of finely-structured ZnO coatings as active layer responsive to CO_2 gas and UV light.

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1. Introduction

Continuous research and development activities are being pursued in fabricating sensors that are able to detect harmful gases in low concentrations, as well as UV light which is used in many commercial fields. Metal-oxide based semiconductors are given attention because of their efficiency in gas and photo-voltaic applications [1-2]. Moreover, nanostructured and porous coatings as active layer are well-known for obtaining high performance sensors from the viewpoints of gas diffusion and active sites. Among metal oxide semiconductors, zinc oxide (ZnO) is a basic sensing material because of its wide band gap and straight forward crystal growth formation [3-4]. The gas sensing activity relies on the surface interaction between the metal-oxide active layer and the target gas molecules [1]. In particular, the chemical composition, crystal structure and the coating microstructure of the active layer are known to greatly influence the response and sensitivity and stability. Meanwhile, the UV detection mechanism of ZnO is regulated by the chemisorption of oxygen [5-6]. In the absence of UV light, oxygen molecules get adsorbed on the surface as negatively charged ions creating a depletion layer. When ZnO is illuminated with UV, electron-hole pairs are generated in where the adsorbed oxygen ions combine with holes to produce oxygen molecules. The oxygen then gets readsorbed on the surface until equilibrium is reached after exposing to UV light [7].

Different complex methods have been applied to obtain ZnO thin films and coatings, e.g., chemical deposition, spray pyrolysis, low pressure metal organic chemical vapor deposition (MOCVD) and rf magnetron sputtering [8-11]. An emerging deposition process called solution precursor plasma spraying (SPPS) could be an alternative to the current complex and expensive ZnO deposition processes [12-13]. SPPS is a straightforward deposition technique which has the ability to develop thin and nanostructured coatings with variable porosities.

In this contribution, ZnO nanostructured coatings are fabricated using SPPS process as active layer for carbon dioxide and UV light detection. The influence of using different starting solution precursors to the coating microstructures is studied. In addition, the electrical, gas and UV light sensing properties are investigated and are correlated to the microstructures of the obtained coatings.

2. Experimental Approach

2.1 Preparation of zincate solution

The zincate solutions were prepared using zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, *Sigma Aldrich, Saint-Louis, Missouri, USA, 98% purity*) and zinc acetate dihydrate *($Zn(CH_3COO)_2 \cdot 2H_2O$, Sigma Aldrich, Saint-Louis, Missouri, USA, 99.99% purity*) as precursors. Appropriate amount of acetate and nitrate salt was dissolved in distilled water and was constantly mixed in ambient condition for 1 hour using a magnetic stirring apparatus. For both precursors, 2.0 M aqueous zincate solutions were prepared and were used for all spray experiments.

2.2 Plasma spraying of ZnO coatings

The plasma spraying of ZnO coatings was performed using SG-100 torch *(Praxair S.T., Indianapolis, IN, USA)* mounted on 6-axis ABB IRB 140 industrial robot *(Zürich, Switzerland)*. The primary gas used was argon at a flow rate of 45 slpm and hydrogen as secondary gas at a flow rate of 5 slpm and were kept constant in all spraying experiment. A continuous stream of solution was fed into the plasma jet by mechanical injection system using an external injector (nozzle). The diameter of the injector was 0.3 mm and oriented 30° between the axes of the injector and of the torch. The coatings were deposited on a F60 sandblasted stainless steel substrate (ϕ = 25 mm, thickness = 3.0 mm). A torch speed of 1000 mm/s and a spray distance of 40 mm were used for all the spraying experiment. The robot which holds the torch was programmed to follow a rectangular spray pattern with 3.0 mm off-set distance after each spray scan for all spray runs. The temperature at the surface of the substrate during spraying was monitored using Impac IN 5 pyrometer (*LumaSense Technologies, Santa Clara, California, USA*).

2.3 Microstructural characterization

The micrographs of the surface and cross-sections of the ZnO coatings were obtained using JEOL MEB IT300 LV (*Japan*) scanning microscope. X-ray diffraction data of the coatings were obtained using D8 ADVANCE *(BRUKER, Massachusetts, USA)* diffractometer under Bragg-Brentano configuration with Cu $K_{\alpha 1}$=0.15406 nm radiation. A continuous scan mode with an increment of 0.02° (2θ) in the scanning range of 20° – 100° (2θ) was used and the resulting diffractogram was analyzed using *Diffrac+EVA Software*

equipped with JCPDS-ICDD database for phase analysis.

2.4 Sensing experiment

2.4.1 Electrode preparation

For the investigation of the electrical characteristics of the ZnO coatings, the two-probe electrical method was used as shown in Figure 1. First, the samples were glued in a glass substrate which serves as the sample's support. Using a conducting paste, the electrical wires were pasted in the sample's surface to create a connection on the sample. On the other hand, the non-conducting tapes were used as support for the electrical wire to avoid connection loss. After drying, the samples were then connected to a National Instruments (NI) I-V curve tracer for electrical and sensing measurements.
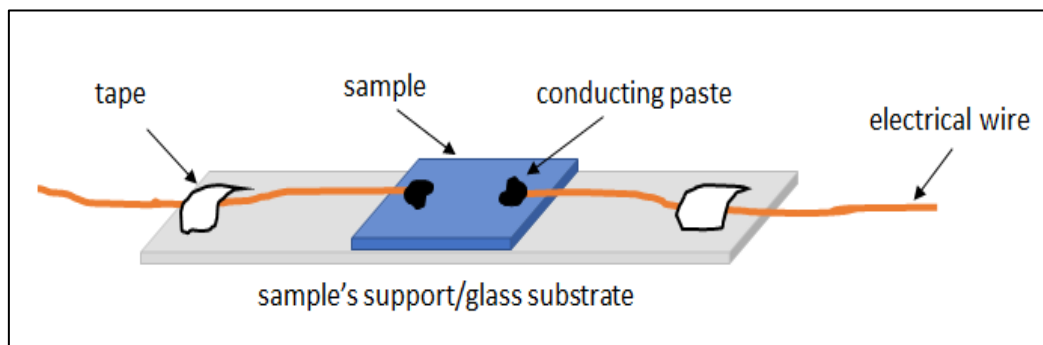

Figure 1: Schematic representation of the sensor prototype with electrodes for sensing test.

2.4.2 Carbon dioxide (CO_2) gas sensing measurement

As depicted in Figure 2, the sensor prototype was placed inside a closed box where the CO_2 gas flows in and out for a given time. The gas tube that connects to the CO_2 gas tank is connected to the entrance hole of the box enclosure, while another gas tube (with scrubber) is connected to the exit hole which then exits to the window. The electrodes were then connected the NI I-V curve tracer for gas sensing experiment. In the measurement, the electrical characteristic was first observed in a free analyte gas condition for 30 seconds as initialization time. After initialization, the CO_2 gas was allowed to flow in the enclosure also for 30 seconds and switched off back for 120 seconds to check the recovery and stability. The CO_2 gas was allowed again to flow for another 30 seconds and then stopped for another 120 seconds indicating another cycle.
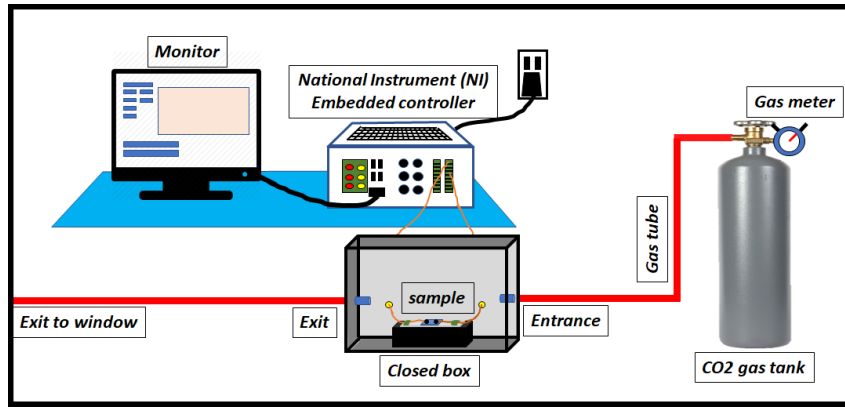
Figure 2: Schematic diagram for the CO_2 gas sensing experiment.

2.4.3 Ultraviolet (UV) light sensing experiment

As shown in Figure 3, the prepared sample was also placed inside a closed black-box containing the UV lamp. The UV lamp has a wavelength of 365 nm corresponding to energy, $E = 3.40$ eV. The electrodes of the prototype sensor were connected to the NI I-V curve tracer to measure the response of the sample to UV light. In the measurement, the electrical characteristic is first observed in a dark condition for 10 seconds as initialization. Then, after initialization, the UV lamp is switched on also for 10 seconds and switched off back for 10 seconds. The process of switching on and off the UV lamp is repeated four (4) times, each for 10 seconds.
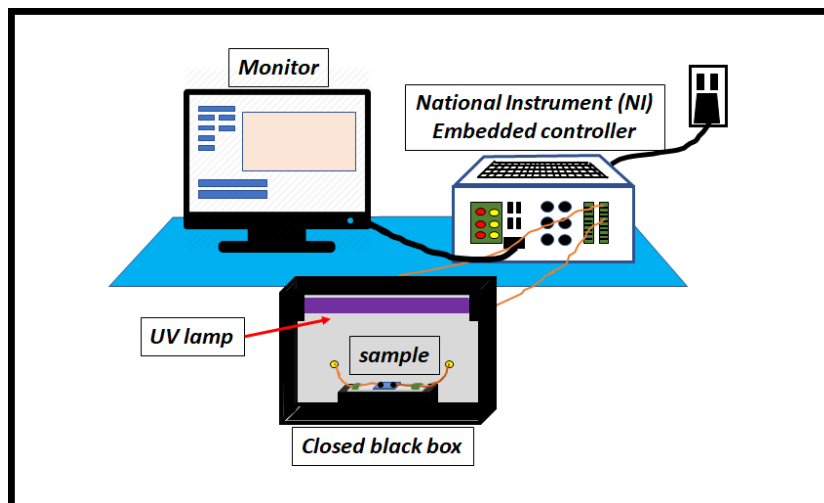

Figure 3: Schematic diagram for the UV photo detection experiment.

3. Results

3.1 Microstructural characteristics of coatings

The X-ray diffraction diagram of the coatings prepared from zinc acetate (Zn-Ac) and zinc nitrate (Zn-N) precursors is presented in Figure 4. The diffractograms revealed the formation of polycrystalline ZnO having a wurtzite crystal structure as indexed using a standard diffraction file (JCPDS 36-1451). The presence of austenitic phase which is attributed to the stainless steel substrate used is due to the thin thickness of the coatings. As observed, there is no significant difference in terms of the peak broadening and phase composition when using different starting solution precursors. In addition, both coatings have predominantly preferred orientation along the (101) plane.
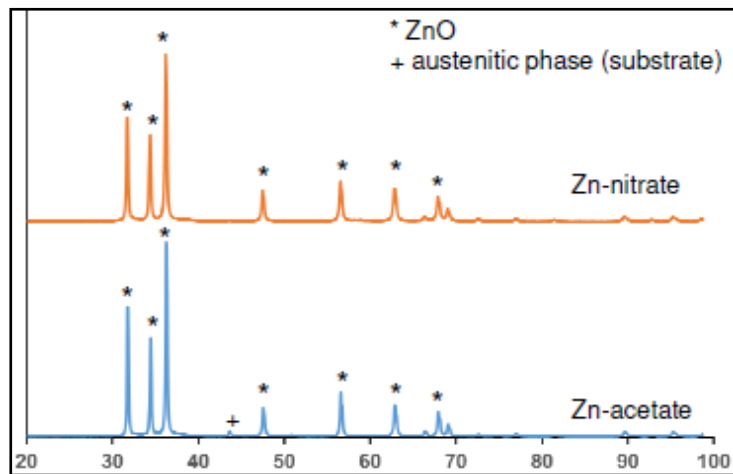

Figure 4: X-ray diffraction diagram of SPPS ZnO coatings prepared using acetate and nitrate precursors.

The surface morphology of the coatings is presented in Figure 5, both in low and high magnifications. The coatings prepared using acetate precursor exhibited relatively smoother and finer microstructural features which are uniformly distributed across the substrate area as compared to that of the coatings prepared using nitrate precursor. The former is generally comprised of very fine spherical particles while the latter tends to form clustered agglomerated or island-type particles.
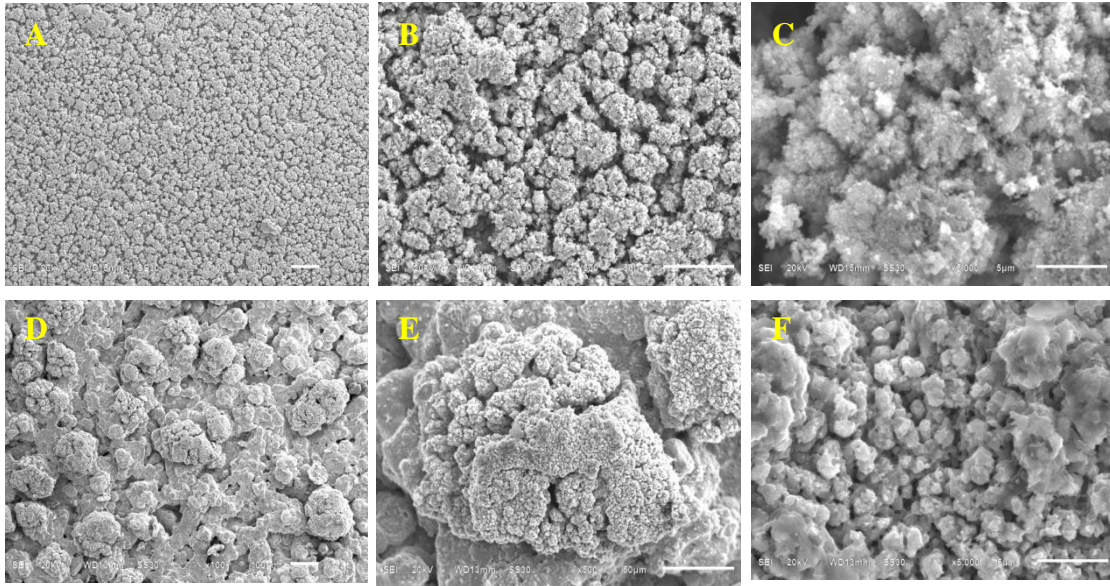
Figure 5: Surface images in low and high magnifications of Zn-Ac coating (a-c) and Zn-N coating (d-f) showing the characteristic microstructures of SPPS coating.

On the other hand, the corresponding cross-section micrographs of the coatings are shown in Figure 6. It is observed that the Zn-Ac coatings is relatively porous and are interconnected than the Zn-N coatings. These pores together with the particle size are expected to play a role in the sensing properties of the coating. Presence of cracks at the substrate-coating interface is observable which can be attributed to the cold nature of the substrate during spraying.
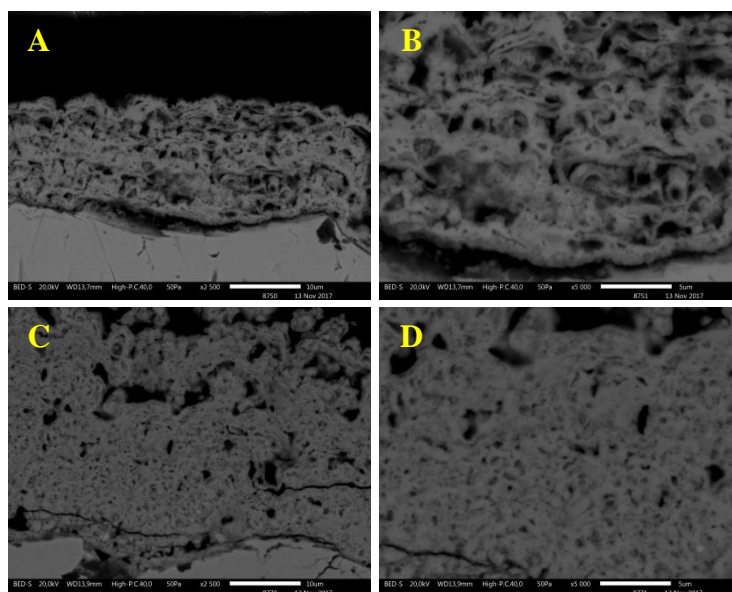
Figure 6: Cross-section images in low and high magnifications of Zn-Ac coating (a-b) and Zn-N coating (c-d) showing the porosity and cracks.

3.3 Sensing properties

3.3.1 CO_2 gas sensing behaviour

Figure 7 is the sensitivity-time curve of the fabricated ZnO coatings to analyte carbon dioxide (CO_2) gas. It can be found that ZnO coating from Zn-Ac precursor has better response to CO_2 gas than the one prepared from Zn-N precursor. This could be related to the microstructural characteristics of the coatings in where the more porous structure has better CO_2 gas detection due to enhanced gas diffusion. Although the ZnO coatings are responsive to CO_2 analyte gas, their recovery over a considered time cycle is very poor or no recovery at all as evidently seen in Figure 7. It is understood in this case that the interaction between the coating and analyte gas is chemical nature and occurs on the coating's surface, but due to the porous attributes of the coatings, the diffusion of CO_2 inside the coating's microstructure may have a big contribution for this no recovery effect. This is clearly observed in "OFF" conditions or no flow of CO_2 gas for both coatings but the signal is still going up. Moreover, it is observed that Zn-Ac coating has quicker response time of ~5 seconds than the ~15 second's response time for the Zn-N coating.
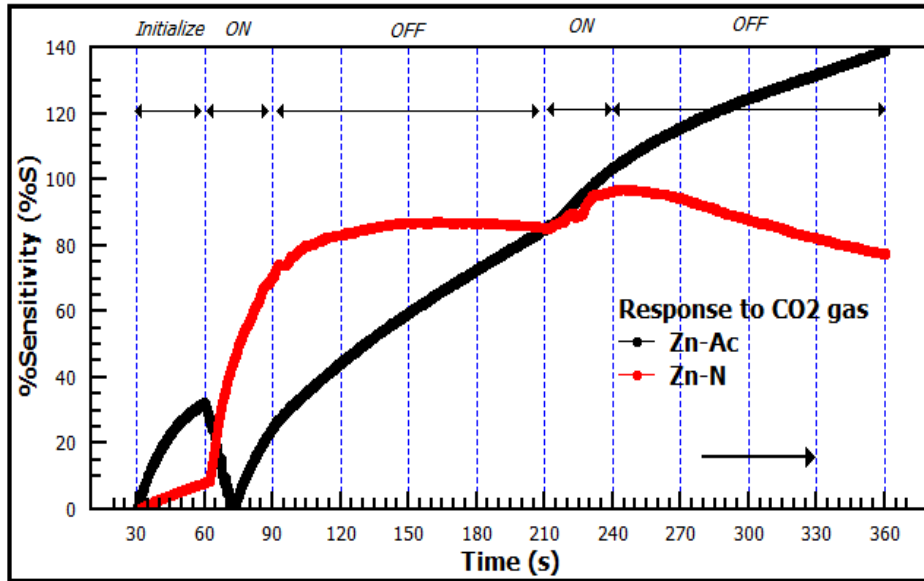
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Figure 7: Sensitivity of as-prepared ZnO coatings to CO_2 gas in terms of percent sensitivity vs. time (%S-t) characteristic: (black) Zn-Ac and (red) Zn-N.

3.3.1 UV light detection characteristics

Unlike the CO_2 gas sensing, the UV light detection of the fabricated ZnO coatings is electrical in nature. As shown in Figure 8, the ZnO coatings are very responsive to UV light and have good recovery characteristics. The ZnO coating from Zn-N precursor is seen to have higher photo detection than the one prepared from Zn-Ac precursor. However, the photo detection of Zn-Ac coating shows steadier behaviour which is desirable characteristic of a photo sensor. These properties could again be attributed to the microstructural characteristics of the coatings in where the more relatively denser ZnO coating prepared from Zn-N precursor has higher generated photo-current than the relatively porous ZnO coating from Zn-Ac precursor. Moreover, the calculated band gap energy of the obtained coatings from both precursors is smaller than the energy of the UV lamp as shown in Figure 9. These values were calculated from the absorption spectra of the coatings.
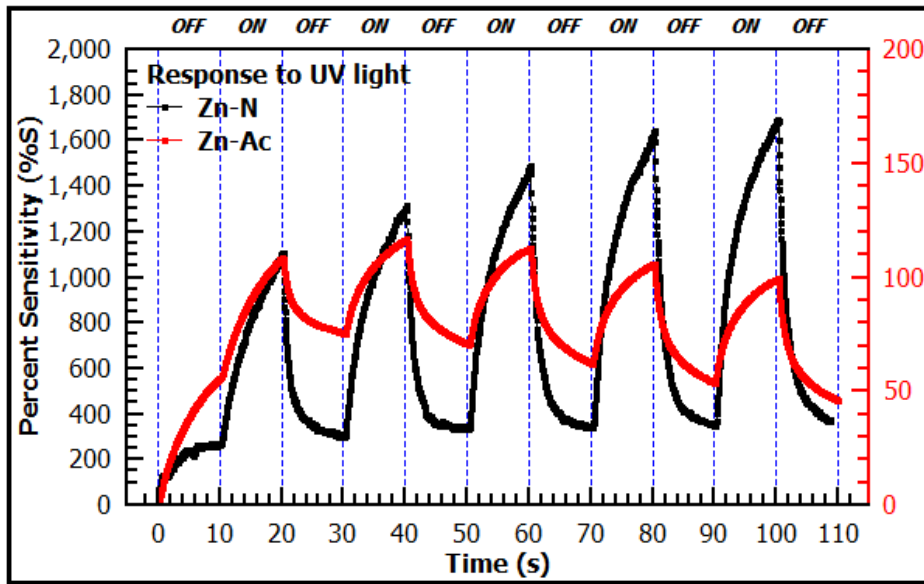
Figure 8: Time dependent response of as-prepared ZnO films to UV light in terms of percent sensitivity vs. time (%S-t) characteristic: (black) Zn-Ac and (red) Zn-N.
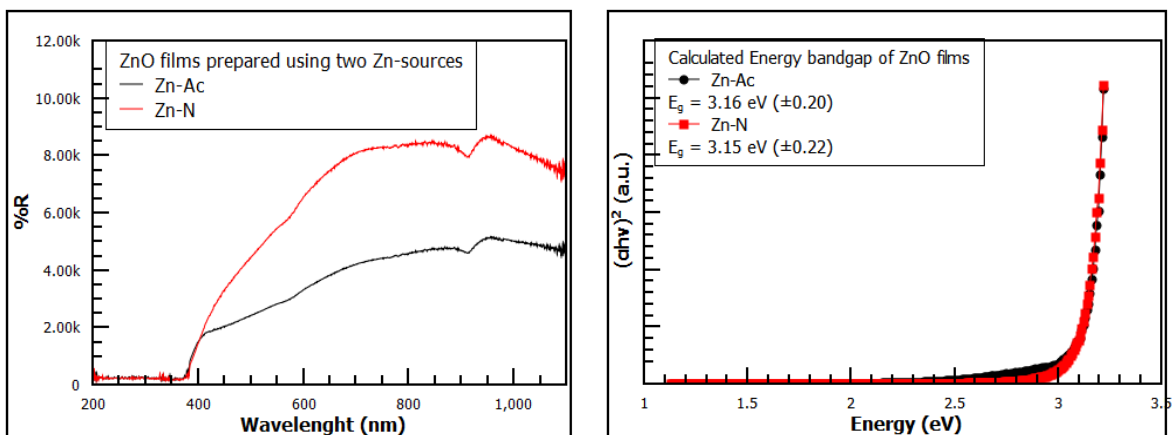

Figure 9: Absorption spectra of both coatings (left) and their corresponding calculated band gap energies (right).

The photo-current decay of the representative coating from Zn-Ac precursor obtained in one cycle is shown in Figure 10. A low decay time constant of 26 seconds is observed which is due to the faster evacuation of charge carriers.
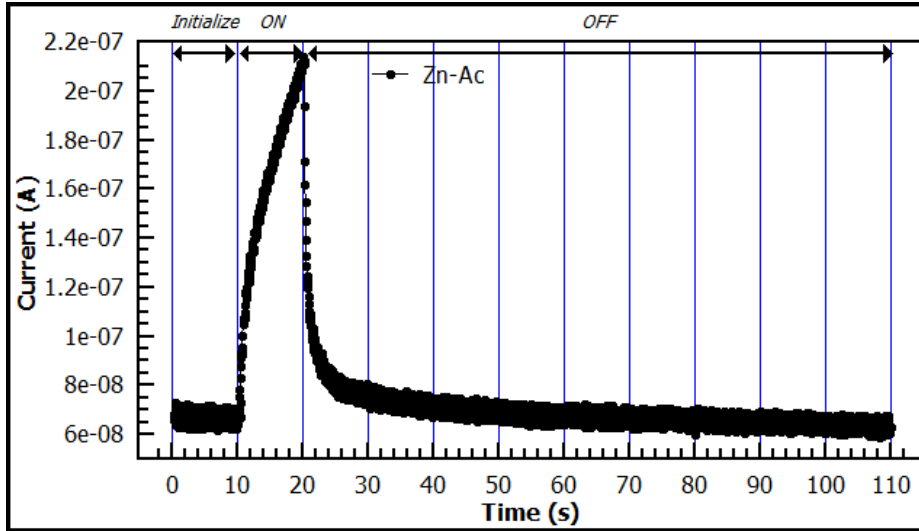
Figure 10: Once cycle decay curve of ZnO coating prepared from Zn-Ac precursor.

4. Discussions

4.1 Precursor influence on microstructures of coatings

Zinc nitrate is a known salt of nitric acid and zinc oxide. Using water as solvent in dissolving this salt, it gets ionized resulting to zinc ions and nitrate ions. The dissociation is simple and can be represented by the following reaction [14]:

$$Zn(NO_3)_2 + H_2O \rightarrow Zn^{2+} + 2NO_3^- + H_2O \tag{1}$$
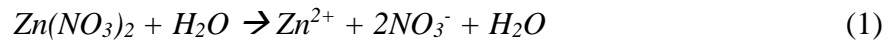
Upon injection of the zincate solution in the high temperature plasma jet, the solution droplets rapidly forms crystallites in random directions that resulted to the formation of island-type surface morphology as shown in Figure 5.

On the other hand, zinc acetate is a salt of zinc oxide and weak acetic acid and has a complex reaction upon dissolution. Dissolving zinc acetate in aqueous solvent partially hydrolyzes it and the rests are ionized. The hydrolysis results in the formation of basic zinc acetate which upon solvent evaporation does not really produce pure zinc acetate but with basic zinc acetate, acetic acid and its ionic derivative. This can be expressed as follows [14]:

$$2Zn(CH_3COO)_2 + H_2O \leftrightarrow Zn(OH)(CH_3COO) + CH_3COOH + Zn^{2+}2CH_3COO^- \tag{2}$$

But during plasma spraying, the interaction of the acetate solution droplets to the plasma jet could rapidly evaporate the solvent and acetic acid resulting to the formation of zinc hydroxide which may be presented as:

$$Zn(OH)(CH_3COO)_2 + OH^- \rightarrow Zn(OH)_2 + CH_3COO^- \tag{3}$$
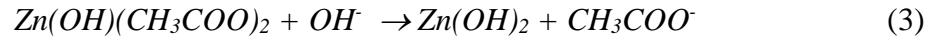
Further heating of the droplets, especially during the subsequent spray passes could result to the formation of pure ZnO particles deposited on the substrate. This can be expressed by the following chemical reaction:

$$Zn(OH)_2 + CH_3COO^- \rightarrow ZnO \tag{4}$$
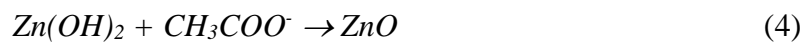
Based from the above chemical reactions, it can be said that the nature of chemical precursors and their chemical reaction when in contact with plasma jet directly influence the microstructure of the ZnO coatings. The complex route of ZnO formation in the case of acetate used as precursor might be one reason of having a porous microstructure whereas the direct and simpler ZnO synthesis route (rapid particle formation) when using nitrate as precursor could be a factor for having a relatively denser coating microstructure. Moreover, these differences are further confirmed with the different particle sizes of the deposits. The coatings from acetate precursor have smaller particle size than the coatings obtained using the nitrate precursor. However, it is noted that the coatings from both precursors crystallizes under hexagonal structure and have preferred orientation along the (101) crystallographic plane as shown in Figure 4. Accordingly, this preferred orientation is the most energetically favourable growth direction as the stacking of particles is deemed to be easier after each spray pass [15].

4.2. Microstructure influence on sensing properties

The processing or synthesis route was viewed to be a crucial factor to the characteristics of the coatings microstructure as discussed in the previous section. Varying the coating's microstructure could result to different response characteristics for a particular sensor material. The obtained ZnO coatings in this work have good response to both CO_2 gas and UV-light which is attributed to high surface area of the finely structured coatings. Having a fine coatings microstructure provides large reaction contact area between the active sensing layer and the analyte material. Although porous microstructure with high surface area is deemed to have better response and stable sensing behaviour than the non-porous one, the ZnO coatings prepared from zinc acetate having percent porosity of 16.2±3.1% coatings and ZnO prepared from zinc nitrate having porosity of 10.0±0.6% showed bad recovery characteristics to analyte CO_2 gas. This can be attributed to interaction of the analyte gas with the inner grains of the ZnO coatings as it diffuses in and out of the coatings. The quicker response time of Zn-Ac coating to the analyte gas than the Zn-N coating is likely due to the quick adsorption of the CO_2 gases to the distributed pores of the Zn-Ac coating.

On the other hand, the ZnO coatings prepared from both precursors have very good response and recovery characteristics when exposed to UV light source which suggest the potential of SPPS-ZnO coating for UV light detection. As sensing is dependent on the reactions at the surface of ZnO coatings, under dark condition, the physically adsorbed oxygen extracts free electrons from ZnO and then creating a depletion region resulting to a reduce conductivity of coating. When exposed to UV light, electron-hole pairs are generated with holes recombining with the adsorbed electrons through the oxygen ions [7]. The electrons generated in the process causes the increase in sensor conductivity and hence, its sensitivity to UV. This mechanism is possible since the energy of the UV lamp (3.40 eV) is much greater than the band gap energy of the coatings (Zn-Ac = 3.16 eV and Zn-N = 3.15

eV) as shown in Figure 9. After exposing to UV light (recovery condition), oxygen gets readsorbed on the surface until no reaction or equilibrium is achieved. This process continues for the next "ON-OFF" cycles as depicted in Figure 8 and this suggests the repeatability of the UV detection mechanism.

5. Conclusion

The current work explored the potential of the solution precursor plasma spray process in fabricating zinc oxide (ZnO) coatings for possible gas and photo sensor applications. It was found that different starting solution precursors resulted to different coatings microstructures. Relatively porous coatings were obtained when using acetate as compared to using the nitrate one which was due to the different chemical route of each precursor when in contact with plasma jet. The obtained ZnO coatings showed good sensitivity and recovery towards UV light. Moreover, they showed also good response towards carbon dioxide (CO_2) gas but does not show any good recovery which was attributed to the coatings' microstructure. These results showed the feasibility of SPPS process for the fabrication of finely-structured ZnO coatings as active layer sensitive to CO_2 gas and UV light at ambient conditions. Testing to different analyte gases and controlling the coatings microstructure are some future works in sight in order to check the selectivity and determine the optimum sensing performance of the coatings.

Acknowledgments

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