Development of functional ZnS nanospheres as active material for acetic acid detection

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Abstract. We have successfully synthesized zinc sulphide (ZnS) nanospheres deposited on glass and silicon on insulator substrates as an acetic acid sensor. Results show that nanospheres deposited on silicon on insulator substrate at lower ZnCl₂ concentration show better response and good recovery. We found out that the sensitivity of the ZnS nanospheres were dependent on the surface morphology and that the morphology is affected by the ZnCl₂ concentrations and the substrates used. Our results show a promising potential of ZnS nanospheres as an inexpensive alternative sensing material to the existing acetic acid detectors.

1. Introduction

Among the dangerous pollutants that can have a compounding long term health effects are the volatile organic compounds (VOCs). Acetic acid (HOAc) is one of the many VOCs widely used in many industries. Large scale industry utilization of acetic acid employs a lot of people who may be exposed to this potentially hazardous organic compound since it is classified as acutely toxic to humans because it is highly corrosive to skin and mucous linings even at 50ppm exposure. Although there are existing methods and materials developed in monitoring acetic acid, however most of these monitoring devices are very expensive and are not good for on-site monitoring. Recently, a variety of sensing materials, such as carbon fiber, graphite, carbon nanotube and boron-doped diamond are employed [1-2] but these materials are quite expensive. One promising material that can be used for acetic acid sensing is zinc sulphide (ZnS) due to its superior chemical and thermal stability, good sensitivity, fast-time response and high selectivity [3] and can be fabricated in a relatively inexpensive way.

Among the various techniques employed in synthesizing ZnS, chemical bath deposition (CBD) is attractive because of its convenient, cost effective and good for large scale application [4]. This method offers an inexpensive fabrication route because it eliminates the need for vacuum conditions and complex equipment.

In this work, the sensitivity of the synthesized ZnS nanospheres deposited on glass and silicon on insulator (SOI) substrates to acetic acid is investigated. Moreover, the effects of using different kinds of substrate and precursor concentrations to the response of ZnS nanospheres to acetic acid as well to its morphology were also explored.

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2. Experimental methods

ZnS nanospheres are deposited on glass and SOI substrates from an aqueous solution using 0.01M and 0.03M zinc chloride (ZnCl\textsubscript{2}), 0.05M urea (CH\textsubscript{4}N\textsubscript{2}O) and 0.3M thioacetamide (C\textsubscript{2}H\textsubscript{5}NS). The total volume is 200 mL by the addition of distilled water. The pH of the solution is maintained at 2.5 by drop wise addition of HCl. The solution is then magnetically stirred at 360 at 70°C temperature for 30 minutes. Subsequently, the substrates are immersed in the solution for three hours to deposit ZnS nanostructures. Current – voltage (I-V) characteristics and sensitivity to acetic acid gas of the ZnS nanospheres are performed via two-probe method inside an improvised gas sensing box for three cycles. Each cycle of exposure and without exposure to acetic acid gas is about three hundred sixty seconds (360 s). The surface morphology and elemental composition of synthesized ZnS samples were examined using JEOL JSM-6510LA Analytical Scanning Microscope.

3. Results and discussions

3.1. Sensitivity and recovery characteristics of ZnS nanospheres to acetic acid

Figure 1 shows the sensitivity of ZnS grown on glass substrate with different ZnCl\textsubscript{2} concentrations under exposure to HOAc gas for three cycles. The sample synthesized using 0.03M ZnCl\textsubscript{2} (sample 3G) exhibits higher response (maximum of ~20% sensitivity) compared to the sample using 0.01M ZnCl\textsubscript{2} (sample 1G) having only a maximum sensitivity of ~9%. The higher response on sample 3G might be due to the agglomeration of the ZnS nanospheres expose to HOAc. It is believed that agglomeration of nanospheres is possible when using higher ZnCl\textsubscript{2} concentration. The presence of the agglomerates might also be the reason in its difficulty in recovering to its original state after exposure to HOAc as observed in the I-V characteristics in Figure 2. On the other hand, the nanospheres grown using 0.01M ZnCl\textsubscript{2} show good recovery which is an essential characteristic for every gas sensors.

![Figure 1](image1.png)

Figure 1. The sensitivity plot of ZnS samples deposited on glass substrate (a) before, (b) during and (c) after exposure to HOAc gas. (red-0.03M ZnCl\textsubscript{2}; yellow-0.01M ZnCl\textsubscript{2}).

Figure 3 shows the graph of the sensitivity of the fabricated ZnS sample deposited on SOI substrate. It is observed that the sensitivity decreases as the concentration of ZnCl\textsubscript{2} is increased and that it has almost the same sensitivity in each cycle. ZnS deposited using 0.01M ZnCl\textsubscript{2} (sample 1S) has higher sensitivity of ~12% compared to ZnS grown using 0.03M ZnCl\textsubscript{2} (sample 3S) having only ~5% sensitivity. Comparing the sensitivity of ZnS nanospheres grown on different substrates using 0.01 concentration of ZnCl\textsubscript{2}, higher response has been observed for ZnS on SOI substrate as compared to ZnS on glass substrate attributed to the less wetting property of SOI substrate. The recovery of the samples were also determined and it was found out that the synthesized ZnS sample using 0.01 ZnCl\textsubscript{2} concentration shows better recovery compared to the grown ZnS sample using 0.03M ZnCl\textsubscript{2}.
Figure 2. $I-V$ curve of ZnS samples grown on glass substrate using different ZnCl$_2$ concentrations showing the good recovery of ZnS using 0.01M ZnCl$_2$.

Figure 3. The sensitivity plot of ZnS samples deposited on SOI substrate (a) before, (b) during and (c) after exposure to HOAc gas. (blue-0.03M ZnCl$_2$; green-0.01M ZnCl$_2$).

Figure 4. $I-V$ curve of ZnS samples grown on SOI substrate using different ZnCl$_2$ concentrations showing the good recovery of ZnS using 0.01M ZnCl$_2$. 
3.2. Surface morphology of the ZnS nanospheres

Micrographs of ZnS deposited on glass and SOI substrates are presented in Figures 5 and 6, respectively. The nanostructures are generally spherical in shape. The morphology of the samples grown on glass substrate revealed grainy structures randomly grouped together forming islands as shown in Figure 5(a). It is observed that compact and well defined nanospheres are grown as shown at higher magnification in Figure 5(b) having average diameter of ~195 nm.

![Figure 5](image)

**Figure 5.** SEM images of the grown ZnS nanospheres on glass substrates using 0.01M ZnCl₂ at (a) 3000x and (b) 27000x magnification and using 0.03M ZnCl₂ at (c) 3000x and (d) 27000x magnification.

However, at higher concentration of ZnCl₂ (Figure 5(c)), dense islands composed of nanospheres that have random sizes and are less defined, randomly covered the whole surface of the substrate. Agglomeration of nanospheres is very apparent at higher magnification as shown in Figure 5(d). This agglomeration is due to the super-saturation of Zn²⁺ ions that add more nucleation sites for other atoms to attach or bind to Zn. This would increase the number of nanospheres that will be adsorbed at the surface resulting to piling up of the uneven distribution of nanospheres. This supports our claim that this is one possible reason in its difficulty in recovering to its original state after exposure to HOAc as observed in Figure 2.

On the other hand, the surface morphology of the ZnS nanostructures grown on SOI revealed uniformly distributed nanospheres as shown in Figure 6(a). At higher magnification (Figure 6(b)), compact and well-defined nanospheres are observed. Additionally, using higher concentration of ZnCl₂ revealed randomly agglomerated nanospheres and less-defined nanospheres forming islands as shown in Figure 6(c). As observed from the SEM images shown in Figure 5 and 6, both substrates revealed that at higher concentration of ZnCl₂ would produce random islands composed of less defined nanospheres that will agglomerate. Higher concentration of ZnCl₂ in the solution will increase the number of Zn²⁺ ions that participate in the nucleation increasing the possibility of collisions between particles as they move randomly. In contrast, ZnS nanospheres grown on SOI substrates are smaller (~152 nm) and uniformly distributed compared to those nanospheres grown in glass substrates even with same concentration of ZnCl₂. The less-wetting property of SOI surface than that of the glass by
water of aqueous chemical bath could be the explanation of the smaller grain size of ZnS grown on SOI. The elemental composition of the grown ZnS nanostructures grown in different substrates is shown in Table 1. It is noted that the Zn to S ratio has a value close to one suggesting that the nanospheres are most purely composed of ZnS. Furthermore, it is observed that at lower concentrations, higher Zn content is present.

**Table 1.** Elemental composition of the ZnS nanospheres with varying concentration of ZnCl$_2$ grown on different substrates using EDX measurement.

| Substrate | ZnCl$_2$ % | % Zn | % S | [Zn]/[S] |
|-----------|------------|------|-----|----------|
| glass 0.01M | 51.04 | 48.96 | 1.04 |
| glass 0.03M | 47.74 | 52.26 | 0.91 |
| SOI 0.01M | 50.78 | 49.22 | 1.03 |
| SOI 0.03M | 50.69 | 49.31 | 1.02 |

**Figure 6.** SEM images of the grown ZnS nanospheres on SOI substrates using 0.01M ZnCl$_2$ at (a) 3000x and (b) 27000x magnification and using 0.03M ZnCl$_2$ at (c) 3000x and (d) 27000x magnification.

4. Conclusions

ZnS nanostructures fabricated as an HOAc sensor were successfully grown on glass and SOI substrates via chemical bath deposition using acidic solution of 0.01M and 0.03M ZnCl$_2$ and is found out to be responsive to HOAc as analyte gas. The surface morphology of the grown samples is
influenced by the concentration of ZnCl₂ and type of substrate used. Agglomerated nanospheres are observed on glass and SOI substrates at higher concentration of ZnCl₂.

It was also observed that the surface morphology would have an influence on the sensitivity of the fabricated ZnS-based sensor. Among the ZnS nanostructures produced, sample deposited on SOI substrate using 0.01M ZnCl₂ showed good response and exhibited good recovery whenever the analyte would be cut-off from the environment. ZnS nanostructures showed good potential as an inexpensive alternative material to current HOAc sensor in the market.

5. References
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