Au Decorated Zinc Oxide Nanowires for CO Sensors

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ABSTRACT

We present the room temperature detection of carbon monoxide using Au decorated Zinc Oxide (ZnO) nanowires. Zin oxide nanowires were grown via Vapor Liquid Solid method whereas the gold nanoparticles were prepared by the solution growth method. Surface of the ZnO nanowires was decorated by Au nanoparticles. Gas sensing properties of such nanowires were studied at room temperature for various concentrations of CO (100 to 1000 ppm) in synthetic air. Enhancement in gas sensing response by Au decoration on ZnO nanowires was observed. Au nanoparticles act as catalyst in chemical sensitization and improve the reaction and response time. The improvement in gas sensing behavior is attributed to the change in conductivity of the metal decorated ZnO nanowires on CO exposure due to the transfer of electrons resulted from gas oxidation at ZnO nanowire surface.

Keywords: ZnO nanowires, Gas sensors

1 INTRODUCTION

Low selectivity and requirement of high operation temperatures for most gas sensors have prompted the use of traditional materials in nanostructured mode. Zinc oxide (ZnO) is an important multifunctional material with applications such as gas sensors, SAW devices, transparent electrodes and catalysts [1-6]. The microstructural and physical properties of ZnO can be modified by introducing changes into the procedure of its synthesis. ZnO has been extensively used as a gas sensing material due to its high mobility of conduction electrons and good chemical and thermal stability under the operating conditions of sensors [7]. For application of ZnO as gas sensors it is preferred that the material be in a controlled size in nanometers. It is well known that the sensing mechanism of ZnO belongs to the surface-controlled type, in which the grain size, defects, and oxygen-adsorption quantities play important roles in sensing response. In several recent reports ZnO nanostructures have been demonstrated to have good sensitivity and it has been shown that the sensitivity and response time of ZnO based sensors strongly depend on the size, specific surface area, and morphology [8, 9].

Nanowires made of ZnO have been considered as ideal building blocks for constructing nanoscale sensors due to their high surface-to-volume ratio and the special physical and chemical properties originating from their size. In recent reports it has been seen that the Au decoration on ZnO improve the ethanol sensing behavior at temperatures above 150^{O}C [10]. In another report Pd decorated ZnO nanowires have been used for ethanol sensing above room temperature [11]. This article is focused on the development of room temperature sensor for toxic gases like carbon monoxide in low concentrations.

2 EXPERIMENTS AND RESULTS

A novel appraoch of developing room temperature CO sensors has been implemented at our laboratory. In order to develop the sensors ZnO nanowires were grown via Vapor-Liquid-Solid (VLS) method and gold nanoparticles were grown from the solution method. ZnO nanowire surface was decorated by Au nanoparticles for developing the sensor material. Complete procedure and mechanism are described below.

(a) ZnO nanowire growth

ZnO and graphite nanopowders in a 1:1 ratio were mixed to form the source weighing of 300 mg for growing nanowires on silicon substrate. Gold has been used as catalyst to growth the nanowires. Si substrate was coated with gold clusters and placed into the quartz tube in furnace [12].

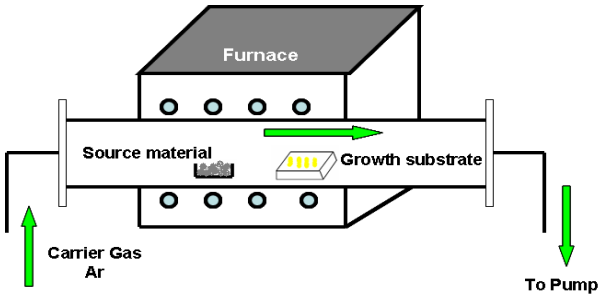

Figure 1 Schematic of the experimental set up for the growth of ZnO nanowires.

The source (nanopowders) and the substrate were loaded in two different alumina boats separated by 2 to 3 cm each.

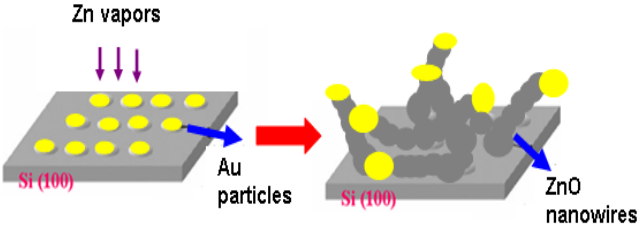

Figure 2 Schematic of the Vapor-Liquid -Solid process.

Source was kept in the high temperature zone while the substrates were placed at a relatively lower temperature in the downstream of the vacuum furnace (figure 1). Zn vapors generated by the reduction of ZnO using graphite at high temperature in argon atmosphere diffuse into the gold clusters, precipitate and then react with ambient oxygen to form ZnO nanowires via VLS growth mechanism. The VLS process is shown in figure 2. The ZnO nanowires were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in figure 3.

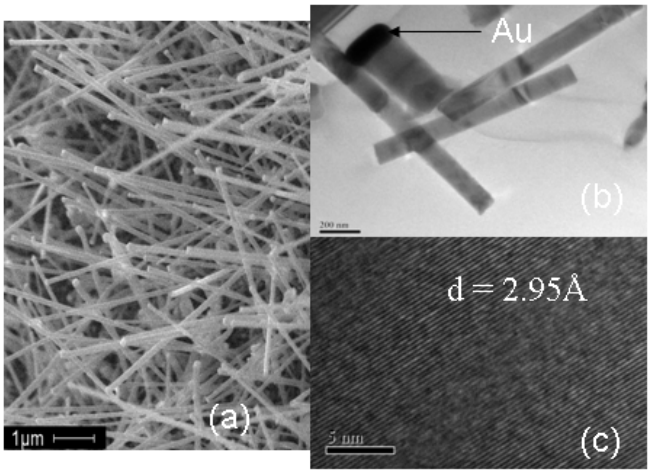

Figure 3 (a) SEM image of the VLS grown ZnO nanowires (b) TEM image for the ZnO nanowires showing Au on the tip as an outcome of VLS process (c) high resolution TEM image for ZnO nanowires showing the d value of ZnO.

(b)Au nanoparticle growth

Au nanoparticles were synthesized chemically using gold chloride solution using the procedure described in reference 13 [13].

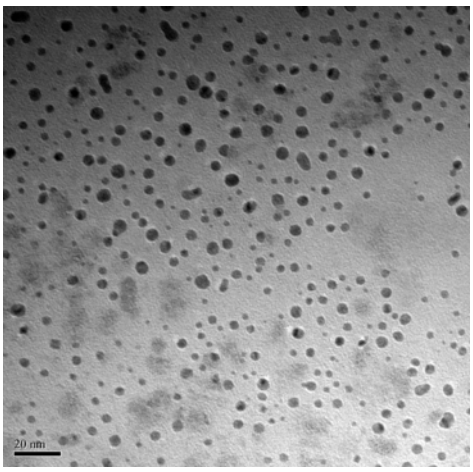

Figure 4 TEM image of the solution grown Au nanoparticles.

$HAuCl_4 \cdot 3H_2O$ (40 mg, 0.102 mmol) was dissolved in deionized water and an appropriate quantity of citrate trisodium salt (100 mg) was added. The solution was refluxed for 30 min and then allowed to cool to room temperature. The resulting reddish solution of the gold nanoparticles was stored in refrigerator for using as catalytic activator to ZnO nanowires. Grain size of the nanoparticles was estimated using TEM. Figure 4 shows the typical TEM micrograph for solution grown Au nanoparticles.

(c) Decoration of Au ZnO nanowires

Chemically grown Au nanoparticles were decorated on the body of the VLS grown ZnO nanowire using solution method. The ZnO nanowires were removed from the silicon substrates by sonification in methanol solution. Fixed quantity of Au nanoparticle solution was added to the ZnO nanowire solution. The resulting solution was mixed properly to allow the deposition of metal nanoparticle on the ZnO nanowires surface using slow stirring of the solution. In order to visualize the Au-decorated nanowires using SEM the gold nanoparticles were directly deposited on the ZnO nanowires on silicon substrate. Figure 5 show the morphology of Au decorated ZnO nanowires. The white spots on the surface of ZnO nanowires are spherical gold nanoparticles in the size range 5-8 nm.

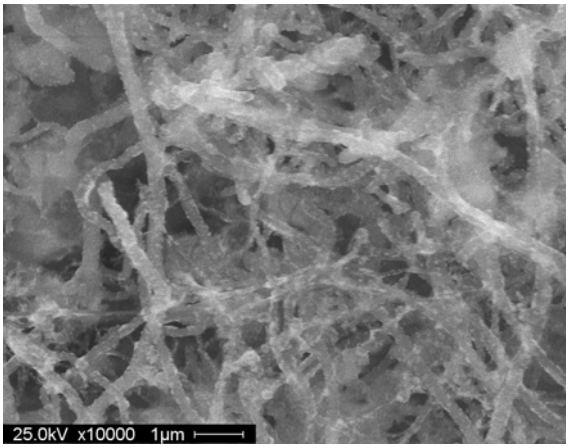

Figure 5 SEM image of the Au decorated ZnO nanowires

(d) Sensor Characterization

Au decorated ZnO nanowires were deposited by using drop cast method on top of the electrodes on the silicon substrate in order to develop the sensor. The electrode geometry is shown in figure 6. The deposition of nanowires on substrate is followed by drying at 100^{o}C in inert atmosphere for the duration of one hr. to get good electrical ohmic contact between the nanowire and electrodes. A proper deposition of the Au- ZnO nanowire on the electrodes shows a resistance value in the range of 4 k Ohm to 7 kOhm. Once the contacts are developed any two of the four electrodes were selected to measure the resistance of the sensor.

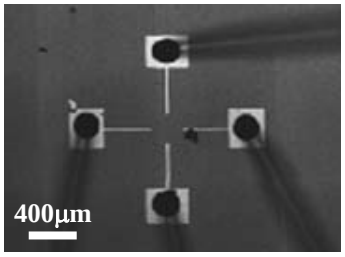

Figure 6 Electrode geometry on the substrate for gas sensor.

3 GAS SENSOR MECHANISMS

The ZnO nanowire sensors were tested for gas sensing behavior by measuring the resistance in presence of compressed air and carbon monoxide using an electrometer *(Keithley 2400)* and a gas controller *(MKS 247).* CO in concentrations of 100 and 1000 ppm mixed in compressed air was purchased from Airgas, Inc, whereas 500 ppm CO concentration was obtained by making a proper dilution of 1000 ppm in compressed air using the mass flow controllers.

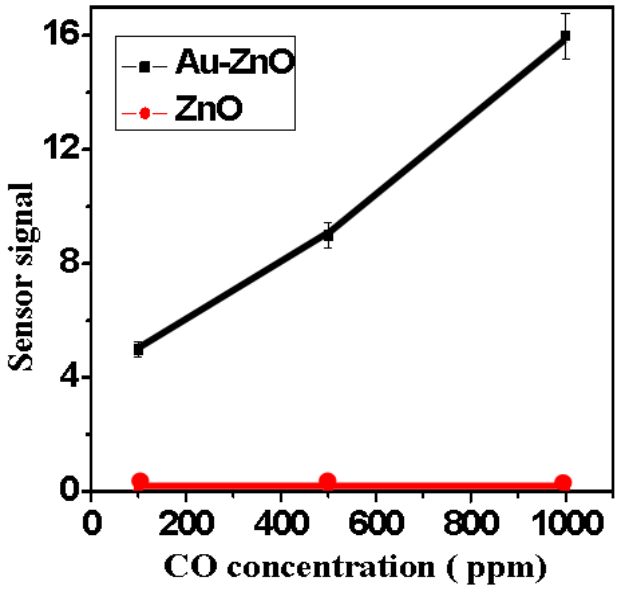

Figure 7 Variation of gas sensor signal with CO gas concentration for ZnO and Au decorated ZnO nanowires.

Carbon monoxide sensing behavior of ZnO nanowire and Au decorated ZnO nanowires based sensors was studied in terms of variation of resistance with time for repeatedly switching of the gas from synthetic air (O_2) to various concentration of carbon monoxide (CO). All the measurements were performed at room temperature. The sensor signal is defined as percent change in resistance of the nanowire film upon CO exposure. If R_a is the resistance in air R_b is the resistance in presence of CO then the sensor signal is defined as $[((R_a - R_b)/R_a) \times 100\%$. There was no change in resistance (~1MOhm) for only ZnO nanowires at room temperatures for any concentration of CO between 100 to 1000 ppm. However, for the Au decorated nanowires we have observed a decrease in resistance for all values of CO concentration. Figure 5 shows show the gas concentration vs. sensor signal $[(R_a - R_b)/R_a) \times 100\%]$ data observed for the nanowire system at room temperature. The gas sensor signal increases with increase of CO concentration whereas the response time decreases. Response time value of ~5 second was observed for 1000 ppm CO in air. Response time is the time needed for the conductance of the gas sensor to obtain 90% of the maximum conductance when CO gas is introduced into anenvironment of air. Based on above results, a mechanism has been proposed to understand this change in resistance by using the basic adsorption chemistry on the surface of the Au decorated ZnO nanowires. It is well known that oxygen sorption plays an important role in electrical transport properties of ZnO nanowires. It is also known that oxygen ionsorption removes conduction electrons and thus lowers the conductance of ZnO. Reactive oxygen species such as O_2^-, O^{2-} and O^- are adsorbed on the ZnO surface at elevated temperatures. It should be noted that the chemisorbed oxygen species depend strongly on temperature and the nature of the material. At low temperatures, O_2^- is commonly chemisorbed. At high temperatures, however, O^- and O^{2-} are commonly chemisorbed, while O_2^- disappear rapidly. ZnO is low conductive semiconductor material therefore the oxygen ionsoption and transfer of electrons is not possible at room temperature. The semiconductor materials should be thermally activated in order to observe the gas adsorption at the surface. This is the reason for not observing any change in resistance while exposing the ZnO nanowires to carbon monoxide. However, on decorating the Au nanoparticles the room temperature gas adsorption can be made possible due to the presence of Au on the surface. Ionsoporion of oxygen ions can occur on gold nanoparticle surface at room temperature due to the highly conductive nature and availability of free electron in gold. The conductive nanoparticle thereafter spills the gas over semiconductor surface via spill over effect [14-17]. The spill over effect via catalytic activation and chemical sensitization is observed to be responsible for room temperature CO sensing by Au decorated ZnO nanowires. The reaction kinematics can be described as follows: CO is a reducing gas and the CO molecule can be adsorbed on Au surface and modify it work function. Initially the reference gas O_2 reacts at the surface of Au catalyst and dissociates into O^-. When the sensor is exposed to CO, the CO molecules on the Au surface interact with the pre-adsorbed oxygen ions. Hence the CO oxidation by gold nanoparticles leads to the the transfer of electrons in semiconducting zinc oxide nanowires in terms of change in resistance of the sensing material. CO oxidation at room temperature and as well as for very low temperatures (below 100K) has been observed and reported for many conductive materials such at Pd [18] , Au

[19] and Ag [20]. In the present Au-ZnO nanowires system the conductance changes when the CO gas is introduced into the test chamber due to the exchange of electrons between ionosorbed species and Au decorated ZnO nanowires.

4 CONCLUSIONS

Metal decorated ZnO nanowires have been used for the detection of carbon monoxide at room temperature. Zin oxide nanowires were grown via Vapor-Liquid-Solid method whereas the gold nanoparticles were prepared by the solution growth method. Gas sensing properties of such nanowires were studied at room temperature for various concentrations CO in synthetic air. Enhancement in gas sensing response by Au decoration on ZnO nanowires was observed. Metal nanoparticles act as catalyst in chemical sensitization and improve the sensing characteristics.

5 ACKNOWLEDGMENTS

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