The Strategy to Control the Morphology of ZnO Nanostructure UV Sensor

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Abstract. The control morphology of ZnO nanostructures at specific area of electrodes by implemented a cost effective fabrication process, is extremely a challenging task. Rapid sensing, fast response and fast detection capability of the electronics devices is nowadays hot subject of keen interest. Our research is one of the successful attempts to achieve the desired goal at certain levels. Therefore in the current research article the ZnO thin film and ZnO nanorods were selectively deposited by low cost sol-gel and hydrothermal growth process at the selective area of microgap electrodes spacing and further the comparative study of ZnO thin film and ZnO nanorods were conducted electrically, for ultraviolet (UV) sensing application. On exposure to ultraviolet (UV) light the current gains, response/recovery times, repeatability, of the ZnO nanorods compared with ZnO thin film was improved probably due to the role of large surface area covered by the deposited nanostructures, and the most important is the bridging nanorods at the microgap electrodes tips. All the characterization including, surface, electrical and structural of the deposited nanostructures were completed by using SEM, sourcemeter and XRD respectively.

Keywords: Micro-gap, Sol gel, Hydrothermal, ZnO thin film, ZnO Nanorods, Ultraviolet light (UV).

1. Introduction
During the last few decades, nanomaterials have been the subject of extensive interest because of their potential use in a wide range of fields like, optoelectronics, catalysis and sensing applications [1-3]. Due to smaller size and larger surface area to volume ratio, nanomaterials exhibits unique properties (physical and chemical) compared to conventional and bulk counterparts [4]. Generally there are three types of nanomaterials (one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D)) have been fabricated [4-6]. Presently, nanomaterials based research areas are rapidly expanding and growing [6]. Moreover metal oxide based nanomaterials have drawn a special attention because of attractive properties coupled with efficient flexibility in structures [7-8]. Physically ZnO ‘Zinc Oxide’ is existed in white powder form. Naturally ZnO exhibit n-type conductivity, while its p-type conductivity can be generated by special synthesis process [8-9].
Generally the semiconductors defects and the numbers of oxygen vacancies plays an important role for the production n-type conduction [9]. There are various methods which has been implemented for the synthesis of nanostructures ZnO, in which the most common are sputtering [9-13], pulsed laser deposition (PLD) [11], chemical vapor deposition sol-gel [12] and metal organic chemical vapor deposition (MOCVD) [13-14] etc. The solution based methods is low cost, simple, need low temperature and also scalable for large areas. ZnO is considering good candidate for electronic device application. Properties of direct and wide band gap allow ZnO to function at high break down voltages, low noise and at high temperature and power [14]. Such characteristics could enhance the application of ZnO for light emitting application mainly blue and ultraviolet light emission diodes [15]. High exciton binding energy (60 meV) of ZnO shows the light emission efficiency at room temperatures [16-17]. Moreover for solar cell technology transparency properties of ZnO allow to use as transparent electrodes [17-18]. To control the nanostructures ZnO at selective area of electrodes is one of the challenging task and less reported. Ultraviolet (UV) photo detector has an important role in military defence system, commercial communication, space communication, environmental pollution, water purification, fire alarm, environmental monitoring, and high temperature flame detection [18]. Therefore the serious conduction of research for the fabrication of low-cost UV sensors is quite necessary so that to control the effect of UV radiation [16]. The measurement of UV radiation is different from visible radiation, because direct optical instrument could not detect UV radiation properly [19].

2. Experimental
To align the nanostructures at desired area of electrodes spacing and, to achieve good resolution during pattern transformation process to wafer samples a chrome glass mask was chosen. The mask containing 22 dies of zero-gap structures. The schematic of such designed can be seen in Figure 1 (a, b, c). The distance between two microgaps was maintained to 15000 μm. P-type 4 inch silicon wafer was selected for device fabrication process. And finally by low cost common mask imaging transfer technique namely photolithography, and by chemicals etching the structure of microgap were fabricated on wafer samples as have been reported previously [21-22, 27-28].

(a) (b) (c)

Figure 1. (a) The AutoCAD design of individual microgap scaled structure (b) Whole mask with different design microgap electrode (c) Original chrome mask with printed microgap structures.

The wet solution, namely sol–gel spin coating technique was implemented to synthesize on oxides substrate, the thin film ZnO. For this purpose the recipe for solution preparation was followed as; Dehydrate zinc acetate plus methoxyethanol-2 was dissolved, while monoethanolamine used as neutralizer, the molar ratio was fixed to 0.5 M. Using RCA1 and RCA2 the wafer samples were washed to remove the dust particles. To create the insulation layer an ~1 μm oxide layer was oxidized on samples by thermal process of oxidation. The metals titanium (Ti) followed by gold (Au) was
deposited using evaporation process. The special designed zero-gap mask was used for fabrication of microgap electrodes by low cost conventional photolithography process. After the gold microgap fabrication the solution of ZnO thin film was dropped on the surface of microcap electrodes by spin coated method with the spinning speed of 4000 rpm for 50 s. and then the coated samples were dried at 250 °C for 10 min on hot plates and were post heated up by using furnace until 350 °C to 1.5 h in the normal air atmosphere. Similarly for ZnO nanorods deposition the recipe for solution was followed as: Zinc nitrate hexahydrate (0.030 M) and hexamethylenetetramine (0.030 M) was mixed in 200 mL of deionised water, and the solution was poured into the 300 mL beaker with a continuous stirring of 30 minutes. Finally the samples were dipped into the mixer with the help of sample holder and were placed in oven for 7 h at 95 °C to achieve the well defined ZnO nanorods. At the end, finally at room temperature the samples were bring out from the oven and then washed out the residual salt from samples by fast nitrogen gas blower. In Figure 2 (a) the schematic of ZnO thin film and in (b) the ZnO nanorods deposition process at the selective area of microgap electrodes can be seen.

By using the SEM (JEOL 5320 LA) the nanostructures deposited samples surfaces were characterised and the structural analysis was conducted by using X-ray diffractometer (XRD Bruker Cu Kα, 1.5406 Å). Finally for electrical measurement the sensors and the meter (Keithly 3400) were placed in series to conduct the current to voltage measurement, followed by switching the UV LED On and Off from 5 V to 5 V bias with respect to steps of 0.5 V. In this experiment the UV LED of wavelength 360 nm and 3 mW power was used for sensing.

3. Result and Discussion
The Figure 3 (a, b) demonstrate the XRD spectra thin film and nanorods ZnO, the spectrums have polycrystalline c-axis oriented peaks. The peaks (100), (002), (101), (102), and (103) shows the uniform perpendicular nature to the surface of substrate. Grain size was calculated from XRD data by using the formula reported in [10]:

\[ D = \frac{0.9 \lambda}{B \cos \theta} \]  

FWHM value is “B” and the bragg angle is denoted by “θ” while “λ” is the wavelength. The grain size was calculated as 32.6 nm while for the ZnO nanostructure lattice constant “c” can be mathematically achieved by implemented the reported formula [11].

\[ n \lambda = 2 dsin \theta \]  

The “n” and “λ” shows the diffraction and wavelength of X-rays, moreover for the miller indices (h, k, l) the spacing is denoted by “d” [12]. This spacing has good relation with the lattice constant “a” and “c” and the Miller indices, which has been reported in following relation [12]:

(a) Schematic of ZnO thin film and (b) ZnO nanorods deposition process at the selective area of microgap electrodes.
The value of lattice constant was calculated as 5.15 Å.

\[
d_{hk\ell} = \sqrt{\frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}}
\]

(3)

The Figure 4 (a) shows the original samples having fabricated microgap structures on silicon substrate. Moreover from the SEM image as shown in Figure 4 (b) we can observe that the surface of the substrate having dense ZnO nano-particles and having roughness, porosity which creates the interconnected particles networks, while in SEM image in Figure 4 (c) the ZnO nanorods provides a bridging networks with electrodes tips.

Both of the two different morphologies deposited sensors were tested electrically under the exposure of ultraviolet (UV) light and studied the effect of photorepose comparatively as can seen in Figure 5 (a) and (b). From the I-V curves we can easily visualize that the ZnO nanorods decorated microgap electrodes has a fast photoresponse as compared with the ZnO thin film probably this might be because of nanorods bridging networks at the electrodes tips.
Figure 5. Current to voltage measurement at UV ON/OFF states of (a) ZnO nanorods and (b) ZnO thin film.

The get more precise measurement for ultraviolet (UV) light photoresponse, current to time (i-t) measurement under ON/OFF states was conducted. From the two different (i-t) curves as shown in Figure 6, we reveal that thin film decorated microgap electrodes have 3 fold higher gain compared with ZnO nanorods by exhibiting rapid response and fast reproducibility which can be verified from the calculated value of repose and recovery timing (1.345 s, 0.132 s), and (2.343 s, 0.234 s), respectively. Finally we can conclude that the ZnO nanostructures deposited samples can be further used for low voltage operating sensors, having rapid response and reproducibility.

Figure 6. Thin film and nanorods current to time (i-t) response curves under ultraviolet (UV) On/off states.

4. Conclusion

The morphology of ZnO nanostructures as thin film and ZnO as nanorods were controlled at selective area of gold coated microgap electrodes by low cost conventional photolithography coupled with wet chemical etching and followed by low cost solution based spin coating technique. All the synthesize ZnO nanostructures measurement was conducted by using XRD and SEM data. Finally the devices were electrically tested for sensing application by conducting a comparative study with respect to ZnO
thin film and ZnO nanorods under the exposure of ultraviolet (UV). The devices were also passed through a current to time (i-t) measurement under ultraviolet (UV) light ON/OFF. Both of the sensors exhibited a fast reproducibility and rapid response at 5 V bias moreover the ZnO nanorods exhibited a fast response probably might be because of bridging ZnO nanorods with electrodes tips. In our upcoming research the microgap size will be improved to nanogap size by implementing a thermal oxidation technique. Then the nano size gap coupled with nanostructure ZnO will be used for biosensing application, by inserting a biomolecules to produce a connecting network with nanostructures, which will definitely improve the sensing of single biomolecule.

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6. References

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