



Original Article

The Enhancement of Visible Absorption of Cu Doped ZnO Nanorods on Patterned Substrates

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Abstract: We report the antireflection and light absorption in visible region by new stretchable substrates with patterned structure. Mogul substrates with 3-Dimensional structures were fabricated by using polydimethyl – siloxane that imitate the nanostructures surface. Then, Copper doped ZnO NRs on mogul-patterned surface by hydrothermal method at low temperature. The optical properties, morphology and structures of ZnO:Cu NRs were investigated through out of measurement the scanning electron microscopy, X-Ray diffraction and ultraviolet-visible spectroscopy, respectively. The results show the Cu doped ZnO NRs were uniformly and dense grown on mogul substrates, well oriented in the (002) plane. Additionally, the light absorption can be significantly enhanced to more 10% in a wide spectral range (400-800 nm) due to the reduce reflection. Growing ZnO NRs doping on new stretchable substrates with a mogul-patterned surface were successfully fabricated and applicable in the flexible and stretchable optoelectronic devices.

Keywords: doping, patterned surface, mogul, ZnO NRs, visible absorption.

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1. Introduction

Optoelectronic devices (ODs) have become an important part of our life. Recently, the development of fabrication and application of ODs are being widely researched. Wherever light is used to transmit information, tiny semiconductor devices are needed to transfer electrical current into optical signals and vice versa. Examples include light emitting diodes in radios and other appliances, photodetector in elevator doors and digital cameras, and laser diodes that transmit phone calls through glass fibers[1].

ODs typically use direct band gap materials such as II-IV semiconductor and light often includes invisible forms of radiation such as gamma rays, X-rays, ultraviolet and infrared, in addition to visible light[1]. ODs are electrical-to-optical or optical-to-electrical transducers or instrument that use such device their operation[1]. The Zinc oxide nanorods (ZnO NRs) are one of the most potential semiconductor materials that used in ODs due to their optical and electrical properties. ZnO NRs are very high absorption in the ultraviolet visible (UV) region, and large surface-to-volume to ratio and variety of morphologies and availability of simple and low cost processing[2]. Currently, many researchers focused studying in this material and applying in ODs such as optical sensor[3], light-emitting devices, flexible electronics and solar cells[4]. However, ZnO NRs has wide band gap (band gap energy = 3.37 eV) and high exciton binding energy of 60 meV at room temperature so absorption incident light at visible region is extremely low[5].

Nowadays, many researches effort to develop ODs such as experimental studies of transition metal doped ZnO have been reported, including studies of doped nanostructures can increase the effective absorption path of the incident light. Commonly used dopants are Co, Ni[6], Cu, Mn[7], and Cr[8]. For examples, Cu doped ZnO photocatalyst thin film were prepared by the sol-gel dip-coating method. This research Cu doped ZnO was fabricated on glass substrates and the result that showed all ZnO which is prepared very high transmittance above 89% in the visible region (400-800 nm). The observed increase in the optical band gap energy as the initial Cu concentration increased was caused by a decrease of the grain size. The decrease of the grain size produced by increasing the dopant concentrations was explained by the pinning effect. On the other hand, Ag was decorated on ZnO NRs substrates to increase absorption in visible region by effect plasmon surface[9,10]. However, the performance and efficiency in this device low and unstable was caused by a fast recombination reaction, response for detector and recovery time still slowly[11]. Additionally, the common problem with doped nanostructures that change of morphology so many research groups have developed various materials and device technologies on stretchable substrates to improve device performance, simple process, low cost and enhance absorption of ZnO NRs. For example, the development of highly sophisticated flexible mobile phones and wearable computing devices or the antireflection and light absorption enhancement by forming sub-wavelength or nano-patterned Si structures via nano-sphere lithography technique[12]. In addition, antireflection techniques, such as modified nano patterned structures and the antireflection coatings, have been used to reduce the reflection loss in order to improve performance[13].

In this work, patterned substrates are replicated by using polydimethyl-siloxane (PDMS) pour on nanostructure surface and the ZnO nanorods (NRs) are grown on these various 3-Dimensional (3-D) structures using hydrothermal method at low temperature to study their optical properties. Various methods have been developed to produce one-dimensional ZnO nano materials, including sol-gel methods, polymer-assisted growth, template-induced growth, solution-liquid-solid growth in an organic solvent, metal-organic chemical vapor deposition (MOCVD) and hydrothermal synthesis. However, the hydrothermal method has many advantages over other method such as relatively simple process, low synthesis temperature, controllable size and low cost[14]. The morphology, structure and optical properties of ZnO NRs grown patterned substrate are investigate by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Ultraviolet-Visible spectroscopy (UV-Vis), respectively. The

results show the high density ZnO NRs, well oriented in the (002) plane and increased absorption in visible region due to the reduction of light reflection on the patterned substrates. The reflection can be reduced to less than 20% and the absorption can be enhanced to more 10%. Growing ZnO NRs on the 3-D structure at low temperature enable the potential applications such as flexible and stretchable optoelectronic devices using visible light.

2. Materials - Methods

2.1. Chemical Materials

Zinc oxide nanoparticles (ZnO NPs) and Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were bought from Sigma Aldrich. Poly(dimethylsiloxane) (PDMS) was ordered from Dow Chemical. Zinc nitrate hexahydrate ($(\text{Zn}(\text{NO}_3)_2) \cdot 6\text{H}_2\text{O}$) and Hexamethylene tetramine (HTM) were bought from Xilong Scientific

2.2. Synthesized process

2.2.1. The cleaner Patterned Substrates

The glass substrates were cleaned by successive ultrasonic cleaning in acetone, ethanol and DI water, for each 20 min to remove grease, soluble organic compounds and other contaminants that could affect the quality of the ZnO NRs from its surface then dried.

2.2.2. Replication of the Mogul-Patterned PDMS Substrate

The base and curing agent is mixed with weight or volume ratio of 10:1. The elastomer PDMS was poured on the patterned substrate and kept in a vacuum chamber to remove any air bubbles. Next, the sample was heated at 80° for 1h30 min that the air bubbles do not return and PDMS film can promptly dry. After that, PDMS was detached from mogul patterned on the glass.

2.2.3. Preparation of ZnO Seed Layers

The ZnO NPs were first dissolved in the solvent ethanol with stirring for completing dissolution. ZnO NPs were diluted to 2% in ethanol. Next, APTES was mixed with the isopropanol. Then, this solution was dropped on the mogul-patterned PDMS substrate that surface of patterned substrates become the hydrophilic. The solution ZnO NPs and ethanol was spin coated at a rate of 3000 rpm for 30s using a spin coater. The as-deposited thin film was heated in an oven at 90°C for 10 min to remove the solvent. After repeating the spin coating and drying procedures for two times to yield the required thickness, the resulting thin film was annealed at 90°C in 30 min to obtain the ZnO seed layer.

2.2.4. Preparation of Cu-doped ZnO Nanorods

After the formation of seed layer, Cu doped ZnO NRs were prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in aqueous of $(\text{Zn}(\text{NO}_3)_2) \cdot 6\text{H}_2\text{O}$ and HMT at room temperature. After the preparation of Cu optimize concentration is 3% by volume, the substrates with a seed layer were put upside down in a glass beaker filled with the above solution, sealed, heated at 90°C for 4h, then cleaned with distilled water and dried at 90°C for 30 min.

2.2.5. Materials characteristics

Morphological characterization and elemental analysis of the NRs were performed in FE SEM S4800 Hitachi. The crystal structures of ZnO NRs are examined in Bruker D8 Advance Powder X-Ray Diffractometer with $\text{Cu } \alpha$ radiation of 1.541 \AA . Optical properties of ZnO NRs grown patterned

substrate are investigated by Ultraviolet-Visible spectroscopy (UV-Vis) by UV-Vis Shimadzu UV-1800.

3. Results and Discussions

3.1. Crystal Structure Cu Doped ZnO NRs

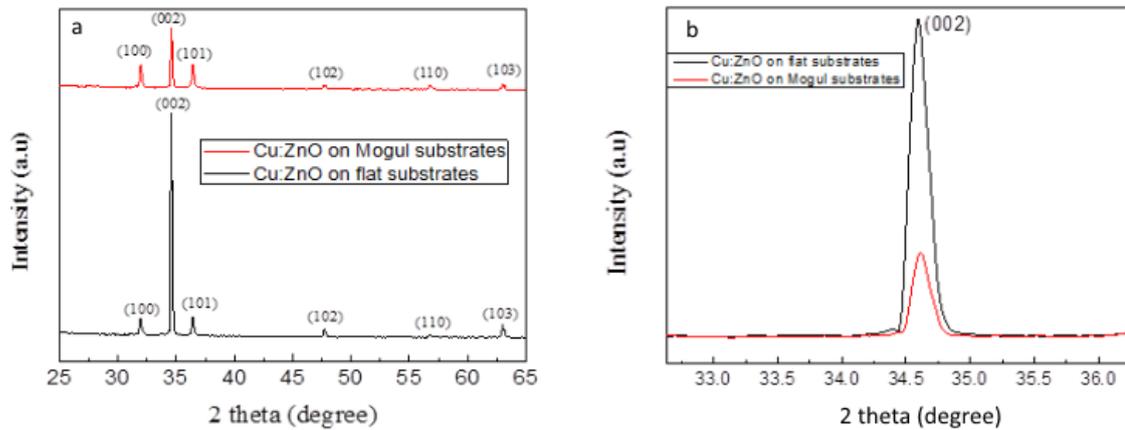


Figure 1. (a) The XRD pattern of Cu doped ZnO NRs grown on the flat surface and patterned substrate. (b) Comparison of the (002) peaks.

Structural characterization of Cu doped ZnO NRs was done by XRD measurement. The crystallite characteristics of these NRs demonstrated the hexagonal Wurtzite structures. ZnO NRs characteristics have six peak that can be seen as 31.76° , 36.21° , 47.59° , 56.76° , which correspond to (100), (101), (102), (110) and (103). The highest intensity of the XRD peak is (002) at 34.4° , which further confirmed the highly crystalline nature of the sample and verifies the NRs growth preferential orientation on the c-axis. It is found that the peak position is slightly shifted towards higher 2θ . The result in Figure 1 shows Cu phases still have not appeared within sensitivity of the XRD which implies that Cu doped ZnO NRs do not still affect to Wurtzite crystallite characteristics structure.

We can see that the intensity of (002) peak on flat substrates higher than that on mogul substrates because ZnO NRs on flat substrates have crystallize better than patterned substrates. Because patterned substrates have wavelength nano-structures so ZnO grain in grow process it can be agglomerate, low crystallization.

The average nano crystalline size was calculated using Debye–Scherrer’s formula through the value of X-ray diffraction spectra[11]:

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta}$$

Where D = crystallite size (nm), k = shape factor (0.9), and β_{hkl} is the full width at half maximum (FWHM-rad), θ = diffraction angle and λ is the wavelength of monochromatic Cu-K α irradiation using in the XRD measurement system ($\lambda=1.541 \text{ \AA}$) [11].

The diameter calculated by Debye-Scherrer’s formula is approximately 38 nm with Cu doped ZnO NRs on flat substrates and that on the Mogul substrates is around 39 nm. The reason for difference size

between various substrates is explained by agglomerate. Pattern substrates have valleys and bumps in a periodic fashion so structures patterned substrates can be seen like the trap. During growth process, ZnO NRs have agglomerate together tendency in hole. This is lead to crystallize grain will priority grow (002) planes so the grains size larger than flat substrates that the crystalline of ZnO NRs not better than flat substrates.

3.2. Morphology of Cu Doped ZnO NRs

Figure 2a shows field-emission scanning electron microscopy (SEM) images of the mogul pattern on the UV- curable polyurethane acrylate (PUA) master mold and the mogul-patterned PDMS replicated by soft lithography from the PUA master mold, respectively. We found the surface topography of the mogul-patterned PDMS replicated from a PUA master mold exhibited the same results as those made directly hat. The stretchable substrate with a mogul patterned surface which can be not only multidirectionally stretchable and versatile for various thin film materials, but also improve the reliability of structures layered on it due to the efficient absorption of applied stress and good adhesion layers on the substrates surface. Additionally, the mogul structure has valleys and bumps in a periodic fashion. Thanks to this structure of mogul substrates, the layers can reduce their stress by straightening out the mogul-pattern stretchable substrates. Figure 2b, 2c presents the top view and cross-section SEM of Cu doped ZnO NRs grown on mogul structure. The depth and breadth of the hole correspond to 50 μm and 100 μm . The high density and uniform of nanorods are displayed in Figure 2d that demonstrated the successful growth of Cu doped ZnO NRs on patterned surfaces.

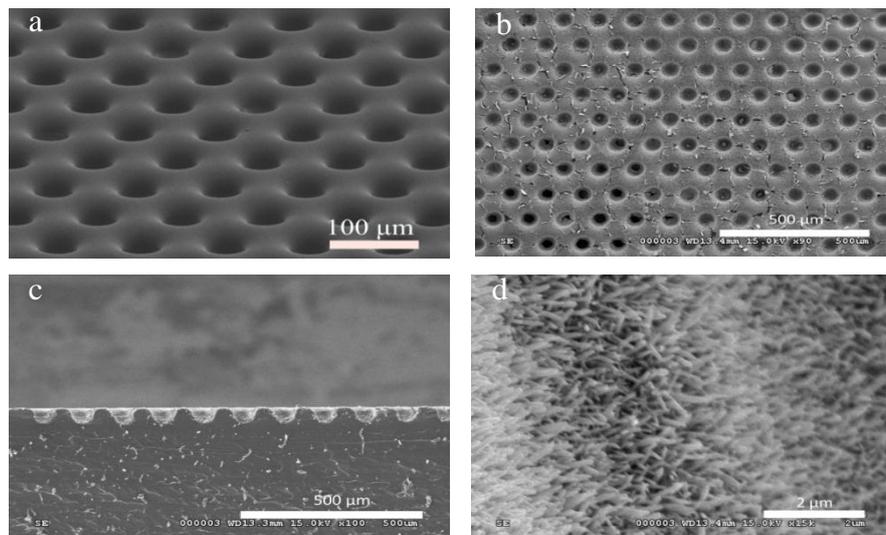


Figure 2. (a)Top view SEM image of stretchable substrates with a mogul pattern, the morphology of Cu doped ZnO NRs array on Mogul substrate (b) top view, (c) cross-section. (d) the large scale of Cu doped ZnO NRs on patterned surface.

3.2. UV-Vis Spectroscopy

The antireflection effect of the nano-patterned substrates was characterized by the calibrated process over a broad wavelength range (400-800 nm). Figure 3a shows the reflection spectra of ZnO NRs on flat substrates exhibits higher than reflection on mogul substrates in the visible light region (400-

800nm). The absorption spectra of mogul and flat substrates can be calculated based on the reflection and transmission measurements. As given in Figure 3b, it is found that the absorption of ZnO NRs on Mogul substrates is significantly enhanced in a wide spectral range (400-800nm). Our results suggest that the patterning substrates formed by the present approach exhibit the good antireflection and absorption enhancement characterization because it provides grading refractive index at the air/PDMS interface. Meanwhile, the optical absorption can be enhanced by using sub-wavelength nano-structures. Since the feature size of surface pattern is smaller than wavelength, the incident electromagnetic wave can couple with the whole surface sub-wavelength structures which can trap the light to enhance the light harvesting in a wide spectral range. Although the aspect ratio is not so high, the good antireflection and absorption enhancement properties reflect their possible application in the future solar cells without introducing a high level of surface defects and low carrier collection efficiency as in the high aspect-ratio structures.

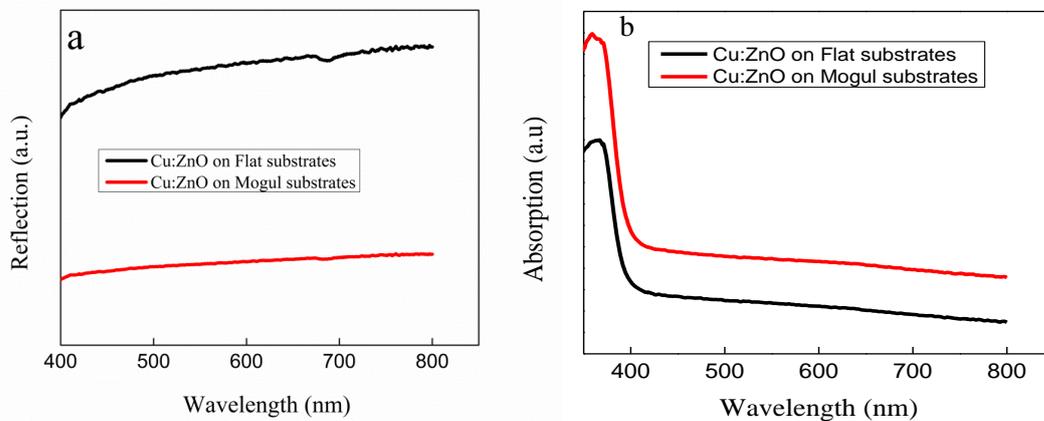


Figure 3. UV-Vis spectra of 3% Cu doped ZnO NRs on Mogul substrates and flat substrates: a) Reflection spectra, b) Absorption spectra.

3.3. Mechanism

Light may be absorbed, transmitted or reflected. When the substrates are illuminated by a signal radiation, some of the light will be reflected, some is absorbed within the material and some is transmitted through it. The Figure 4 shows that light coming to flat substrates is immediately reflected contrary to mogul substrates. The different in light reflection and absorption at flat and patterned substrates can be explained by light trapping which related to wavelength nano-structures on the front of mogul substrates surface. The mogul substrate was designed bumps, valleys and opaque so forces light to bounce more than once on the substrates and thus giving multiple chances to light rays enter the substrates. This happened due to these wavelength nano substrates controls the light's travelling path by changing the angle surface in which light travels, thus giving a secondary scattering and this help keeping absorption losses in the scatters to a minimum before light way back to the air[15]. For glass substrate is thin, glossy surface and transparent and the light only transmit transparent medium. Additionally, when the reflection happened at the interface between the air and surface, the light will be bounce and way back to the air. All factors make absorption light on patterned substrates higher than glass substrates.

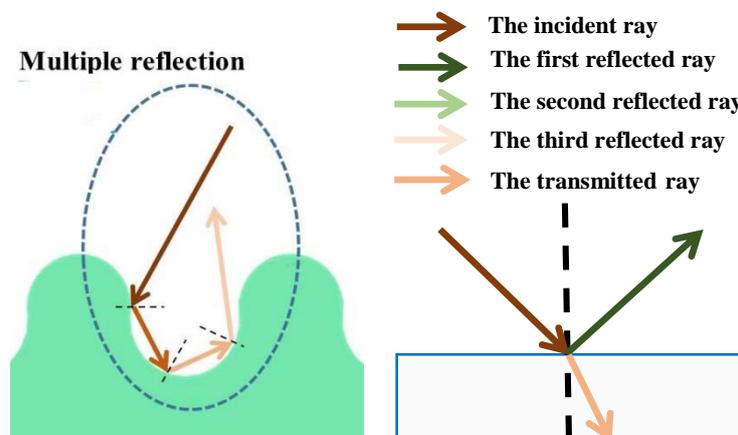


Figure 4. Simulate reflection light on patterned substrates and flat surfaces.

4. Conclusion

In summary, ZnO seeds were uniform formed on PDMS substrates by hydrothermal method, the high density Cu doped ZnO NRs well oriented in the (002) plane. Our results indicated that the ZnO NRs doping arrays coated on patterned substrates were reduced light reflection than PDMS on flat substrates, thus enhanced absorption in visible region. The mean reflection can be reduced to less than 20% and the absorption can increase by than more 10%. Growing ZnO NRs doping on the 3-D structure at low temperature enable the potential applications such as flexible and stretchable optoelectronic devices using visible light.

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