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RESEARCH ARTICLE

Variations in Optical Properties of ZnS/Cu/ZnS Nanostructures Due to Thickness Change of ZnS Cap Layer

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ABSTRACT

Nanostructures of ZnS/Cu/ZnS were deposited on glass substrate using physical vapor deposition technique. The thickness of the first and last ZnS layers was altered, while the thickness of the embedded Cu layer was fixed at 50 nm. The produced nanostructures were of good quality. Spectrophotometric measurements were carried out on the nanostructures to investigate the optical properties. The transmission and reflectivity spectra were recorded and studied in detail. ZnS was selected due to its high refractive index, ease of deposition, and low cost. The copper layer was used because of its low absorption in the visible part of the spectrum and its thermal stability. The ZnS layer was found not only to anti-reflective the Cu layer, but also to stabilize the nanostructure, improve its adherence on glass substrate, and increase the film thermal resistance up to 240 °C. Furthermore, all the samples exhibit good thermal stability up to 240 °C upon annealing for two hours.

Keywords: Optical properties; Transmission, Coating; Annealing, Nanostructures

1. Introduction

II-VI semiconductor structures have recently attracted increasing interest due to the considerable progress in the epitaxy growth techniques. As compared to the relatively smaller band-gap III-V structures, the wider band-gap II-VI compound multilayer structures are more suitable for various optoelectronic devices covering the near-infrared to visible and ultraviolet spectral range. The fabrication of semiconductor thin films with layer thicknesses and chemical composition that can be controlled extremely precisely was an outcome of the recent developments of crystal growth techniques. The optical properties of semiconductors can be altered by varying the layer thickness and composition of the material to meet the specific requirements of the device of interest such as optical filters, light detectors, light emitting diodes (LED), semiconductor lasers, and flat display panels. Studying the optical properties of thin films is considered one of the most important tasks carried out by researchers now days in the field of electronic and optoelectronic devices [1]–[3]. Recently, there has been much attention paid to transparent conductive oxides (TCOs) due to their potential applications in optoelectronics, flat panel displays [4], [5] and solar cells [6]. These systems are used to develop a highly conductive and transparent film to enhance device performance at room temperature. So far, doped oxides such as In_2O_3, SnO_2 and ZnO [7]–[9] have been used. In general, different methods such as thermal evaporation, chemical vapor deposition, spray pyrolysis, sol–gel process, pulsed laser deposition and sputtering have been used for deposition of TCO and metal films on different substrates. Recently, a combination of dielectric, semiconductor and metal were used to fabricate highly transparent conducting oxides. On the other hand, these materials are limited in their application because they are unstable chemically and thermally in various environments [10], [11].

However, the major cost factors, in the production of TCO are the extremely high target cost of ITO [12]. New materials must be developed with lower resistivity than previously achieved and with optical properties superior to those of the present generation. One of the most potential candidates to substitute ITO film is being the ZnS due to its non-toxicity, low cost [13], and hard material capable of withstanding adverse environmental conditions. During the past two decades, Dielectric/Metal/Dielectric films (D/M/D) have been studied intensively. These films are used as spectrally selective filters that reflect the long wavelength IR radiation (due to the properties of the metal layer in them) and transmit most of the visible and near IR part of the spectrum. For these properties, they are also known as 'heat mirrors'. The highly reflective metal film, (that would otherwise be opaque to the visible) is sandwiched between the two dielectric layers that act as anti-reflective coatings: with an appropriate index of refraction and thickness, the light beams reflected on the front and back surface of each of the dielectric layers are of opposite phase and nearly equal amplitude. Thus, they interfere destructively and consequently, the film reflectivity is diminished. By varying the material and thickness of the three layers, the optical properties of the D/M/D films can be tailored to suit different applications.

An attempt has been made in this research paper to show that when a metal mirror layer with high reflection is embedded between two dielectric layers, the dielectric/metal/dielectric multilayer system can suppress the reflection from the metal in the visible region and achieve a selective transparency effect. To reduce both materials and production costs for the D/M/D films, ZnS (with refractive index n~2.3) was chosen to be used as a dielectric layer. The cost of ZnS powder compared to an equal amount of TiO_2 (a material with similar refractive index) of the same purity is about 2.5 times lower. Furthermore, the deposition of ZnS is straightforward: neither substrate heating nor a gas supply is required and a simple thermal evaporation is sufficient for ZnS films of excellent quality [14], [15]. Cu metal films have very good conductivity and suitable for transparent conducting electrode [16]–[18]. ZnS is known to crystallize into two basic structure forms; Cubic zinc-blende and hexagonal wurtzite. On the other hand, ZnS is a direct bandgap semiconductor with the principal band edges occurring at the Γ point (k=0) [19]. In this research work, optical spectroscopic measurements such as transmission and reflectivity are used to investigate the selective transparency effect of the ZnS/Cu/ZnS nanostructures. Furthermore, furnace annealing was used to verify the stability of the nanostructures against heat.

2. Materials and Methods

ZnS/Cu/ZnS nanostructures were prepared using Edwards Auto 306 Physical Vapor Deposition Unit from Edwards Company. First, highly cleaned glass substrates (4x2x0.1 cm high quality glass slices) were used for the preparation of the samples. Pure ZnS and Cu powder (99.99% pure) were used for preparation of the samples. The powder was first pressed at into small capsules to prevent scattering during deposition and then put inside a small boat made of Tungsten (W) inside the PVD Unit. The PVD Unit was cleaned thoroughly to avoid contamination of other elements. A thin layer of ZnS at a thickness of about 70 nm was deposited onto the glass substrates at a pressure of $1x10^{-6}$ mbar using Joule effect. One sample of ZnS/Glass was kept as a reference and the rest were used for the deposition of another layer of Cu onto the ZnS/glass samples at the same deposition parameters and at a thickness of 50 nm. Again, one sample was kept as a reference and the rest were used for the deposition of a third layer of ZnS onto the Cu/ZnS/glass samples. The third ZnS layer was deposited at the same deposition parameters and at two different thicknesses: one sample at a thickness of 90 nm (described as sample ZCZ1) and the other sample at a thickness of 70 nm (described as sample ZCZ2). All the samples were deposited at room temperature. Table 1 shows the thickness of the deposited thin films on the glass substrate for both samples. The thickness of the multilayers was measured using (FTM) films thickness measurement.

Table 1: *Thickness of the deposited layers on the glass substrate for both samples.*

Layer	Thickness (nm)	Pressure (mbar)
Sample ZCZ1		
ZnS	70	$1\text{x}10^{-6}$
Cu	50	$1\text{x}10^{-6}$
ZnS	90	$1\text{x}10^{-6}$
Sample ZCZ2		
ZnS	70	$1\text{x}10^{-6}$
Cu	50	$1\text{x}10^{-6}$
ZnS	70	$1\text{x}10^{-6}$

3. Optical Measurements

The optical measurements of the prepared samples were carried out using Jasco V-570 Spectrophotometer. The transmission and reflectivity spectra of the ZnS/Cu/ZnS nanostructures were recorded. Figure 1 shows the transmission spectra of sample ZCZ1. We notice from the figure that the transparency effect is not seen. This is due to the difference in thickness between the first and last ZnS layer. This can be explained because the destructive interference between the two ZnS layers is not accomplished and the reflectivity is not diminished [14]. Therefore, few peaks are seen in the transmission spectrum of sample ZCZ1 at wavelengths of about 600 nm and 1300 nm. To overcome this problem, the thicknesses of the first and last ZnS layers were adjusted equally. To do this, the deposition parameters were optimized and the thickness was adjusted at 70 nm for both layers.

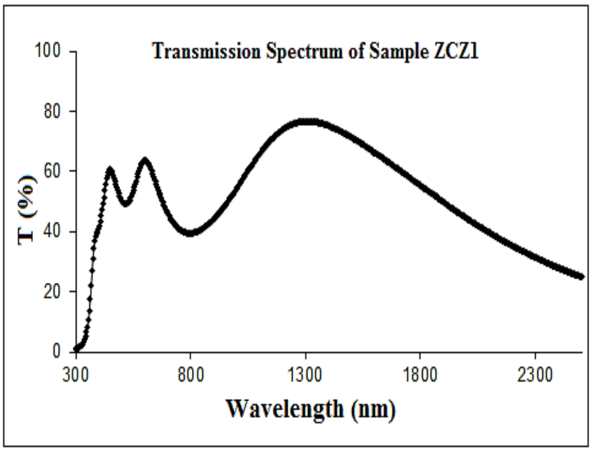

Figure 1: *Transmission spectrum of sample ZCZ1.*

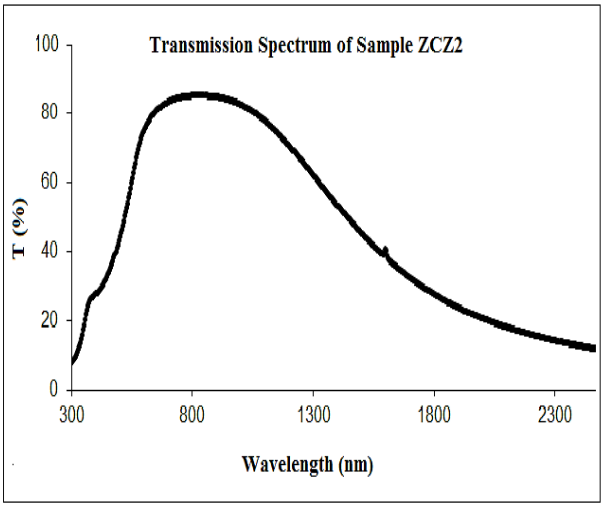

Figure 2: *Transmission spectrum of sample ZCZ2.*

Figure 2 shows the transmission spectrum of sample ZCZ2. It can be seen from the figure 2 that the sample has a good quality and the transparency effect is achieved where most of the visible and near infrared light is transmitted (about 85%) and a decrease in transmission towards higher wavelengths is accomplished which is the real aim of the present work. The reflectivity spectrum of sample ZCZ1 has been represented in Figure 3. The figure shows clearly the incapacity of the nanostructure of being transparent to the visible and near IR part of the spectrum.

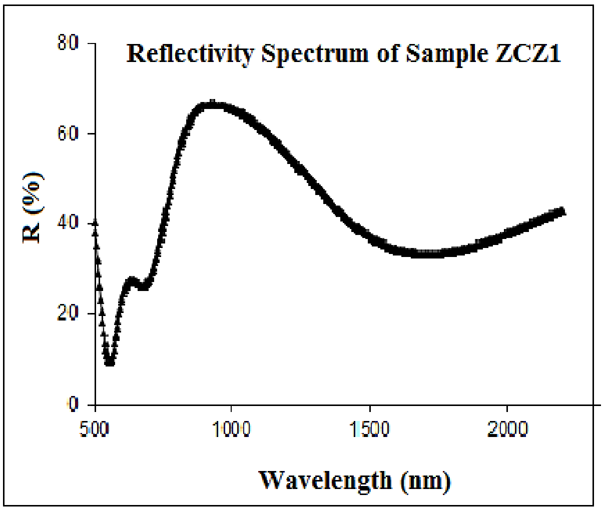

Figure 3: *Reflectivity spectrum of sample ZCZ1.*

On the other hand, Figure 4 illustrate the reflectivity spectrum of sample ZCZ2, which confirms the transparency effect of the nanostructure where a large decrease in reflectivity is noticed in the visible and near IR part of the spectrum and a large increase towards higher wavelengths. Again, this is due to the presence of destructive interference between the two ZnS layers [14].

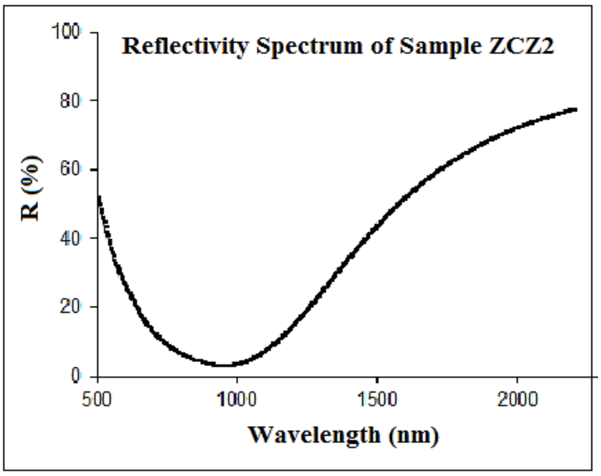

Figure 4: *Reflectivity spectrum of sample ZCZ2.*

To investigate the stability of our structure to heat, all the samples are annealed using Carbolite Furnace with accuracy up to 0.05 °C. The transmission spectra of ZnS/Cu/ZnS nanostructure, at different annealing temperatures of sample ZCZ1 is shown in Figure 5. The stability of the structure is quite good and this due to the tremendous properties of the ZnS and Cu thin films.

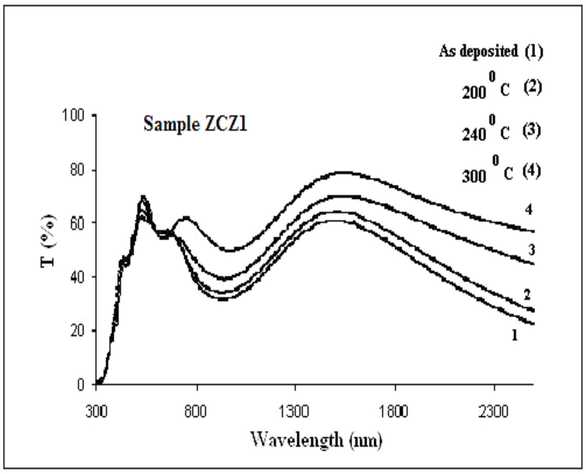

Figure 5: *Transmission spectra of sample ZCZ1 at different annealing temperatures.*

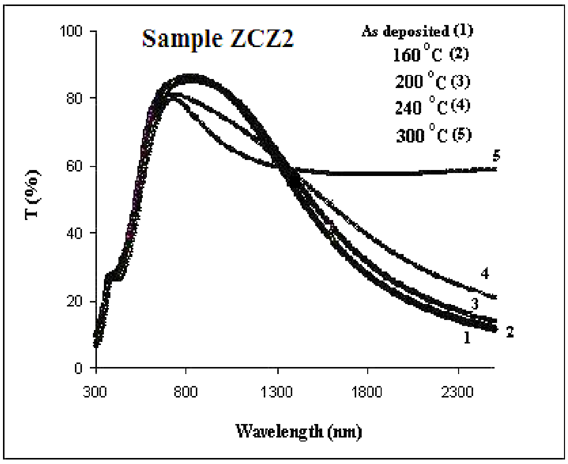

Figure 6: *Transmission spectra of sample ZCZ2 at different annealing temperatures.*

Figure 6 shows the transmission spectra of sample ZCZ2 at different annealing temperatures. The structure of the ZCZ2 sample showed perfect stability up to 240 °C. When the temperature increased to 300 °C, the structure of the ZCZ is destroyed and the transparency effect is lost, where the transmission is increased towards higher wavelengths. This behavior could be attributed to the diffusion of the Cu atoms upon annealing into the two ZnS layers, where probably a modified structure is obtained the transparency is vanished. Because of the annealing process, the surface roughness of the sample is increased due to Cu accumulation, thus, a decrease in transmission is noticed which is attributed to the enhanced surface scattering effect [20].

4. Results and Discussion

From the above experimental data, we found that the choice of ZnS and Cu was quite successful and the transparency effect in the visible and near IR part of the spectrum was very clear. To maintain this transparency, the thickness of the first and last ZnS layers must be equal to accomplish destructive interference between them. The transmittance of the ZCZ2 sample reached a value of 85%, which is good enough as shown in figure 2. When the thicknesses of both ZnS layers are altered, transparency is lost. The option of Cu thin film was victorious due to its low absorption in the visible part of the spectrum and its thermal stability. Moreover, Cu metal films have very good conductivity and suitable for good transparent conducting electrode. The annealing process revealed the good thermal stability and excellent quality of the ZCZ samples. Both annealed samples showed good stability up to 240 °C where the structure of the sample was unspoiled. This stability is lost when annealing temperature increased to 300 °C, and most probably due to the diffusion of Cu atoms from the intermediate layer into both ZnS layers where the enhanced surface scattering effect takes place.

5. Conclusion

Nanostructures of ZnS/Cu/ZnS were deposited on glass substrate. Spectrophotometric measurements were carried out on the prepared samples to examine the transparency effect. The transmission and reflectivity spectra of the deposited nanostructures showed that selective transparency effect is highly dependent on the thicknesses of the first and last ZnS layers. The transparency in the visible and near IR part of the spectrum was very evident in the prepared sample with equal thicknesses of ZnS (sample ZCZ2). On the other hand, the transparency was lost in the sample with different thicknesses of ZnS (sample ZCZ1). In addition, all the samples exhibit good thermal stability up to 240 °C upon annealing for two hours. This stability was demolished upon annealing the samples at 300 °C which is mainly due the enhanced surface scattering effect.

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