ENERGY SAVING OF TRANSPARENT HEATING MIRROR FEASIBLE BY NANOSIZE MULTILAYER ZNS/AG/ZNS COATING

G. Kavei  S. Nikbin
Semiconductors Division, Material and Energy Research Centre, Tehran, Iran
g-kavei@merc.ac.ir, saeedn1986@gmail.com

Abstract- Dielectric/Metal/Dielectric (D/M/D) thin films deposited on glass offers significant energy savings in buildings and can find other applications as components of advanced materials design. ZnS/Ag/ZnS multilayer system for the transparent electrodes in flat panel displays was designed. The optical and electrical performance of an Ag and ZnS single layer films with nano-dimensions were investigated. The smallest thickness of the continuous single layer Ag film that could be deposited on the glass surface is approximately 12 nm. To reduce the complexity and cost of production of ZnS/Ag/ZnS films, physical vapour deposition was used in the laboratory. ZnS was used because of its high refractive index, ease of deposition and low cost; Ag was used because of its low absorption in the visible spectrum. The films produced were of good quality, with luminous transmittance as high as 83.9% and IR reflectance above 90%. The spectroscopic ellipsometry analysis indicated that the interlayer between the Ag and ZnS layer contains a physically mixed layer and a compound semiconductor layer. Based on these studies, according to the characteristic matrix theory, the design for the optimized system was carried out with complete searching strategy. The optical properties of the films designed were also predicted and the most suitable materials were identified. The optical properties of the films produced were measured and were found to compare favourably with the theoretical predictions.

Keywords: Heat Mirror, Energy Saving, ZnS, Spectroscopic Ellipsometry (SE), Electron Beam Vapor Deposition Technique.

I. INTRODUCTION

Windows and related glazing elements are essential components of passive solar systems. Architecturally, a window is a very complex building component which must perform multiple, often contradictory, functions. In order to function effectively in a passive solar heating role and maximize beneficial heat gain, the window must be highly transparent to the incident solar spectrum but must also have a high resistance to all thermal loss mechanisms. One approach to reducing thermal losses while maintaining high solar transmission involves the use of thin, transparent optical films which are reflective to the long-wave infrared radiation (low emissivity) emitted by room temperature surfaces. These thin films, known as “heat mirrors”, can be applied to glass or plastic glazing material, and depending on the application, will reduce thermal losses by 25-75%.

Zinc sulphide (ZnS) is one of the candidates used as thin film and an important II-VI semiconductor material with a wide direct band gap $E_g = 3.65$ eV (bulk), [1]. Many commercial optical products, such as optical fibers, scintillators, integrating spheres, calibrating spectrophotometers, window blinds, luminaries, reflective panels, etc., require highly efficient diffuse reflective surfaces that can withstand temperature and light illumination, [2-3]. Such surfaces can be constructed using a reflective coating on the substrate, [3-4]. The coating protects the substrate from degradation and also serves as a light reflector.

The reflective coating formulation usually contains a number of components. A primary component is reflective pigment, which imparts a pleasing color and reflective properties of the various media in which it is mixed, such as paints, organic resins, varnishes, etc. A secondary component is a binder, which can be natural or synthetic, used to bind the pigment to a substrate and to provide durability to the coating. In addition, most coatings require a solvent, which is used to disperse the pigment and binder for the easy application of the coating material to a substrate, [5].

In recent years, an increasing concern of environmental issues of emissions, in particular global warming and the limitations of energy resources has resulted in extensive research into novel technologies for generating electrical power. Extensive investigation of energy saving e.g. energy savings potential by using green roofs [6] or solving dynamic economic dispatch including practical constraints and renewable energy source, [7] carried out. Many other attractive topics also are available to study as an alternative green energy generator.

An energy-efficient window is a device capable of providing lighting and thermal comfort at minimum demand of paid energy (air conditioning in summer). In a warm climate overheating from excessive solar input is a problem [8]. However there are different ways to use this solar input as an energy source for solar cells [9], collecting energy for cold region [10] or other kinds of energy utilization.
High energy efficiency obtained using multilayer thin film-coated glass windows called heat mirrors that are transparent to visible light and reflecting for infrared (IR) solar radiation. A three-layer system of dielectric/metal/dielectric (D/M/D) on a glass substrate could be used as a spectrally selective filter that reflects IR radiation and transmits most of the visible spectrum. The D/M/D were fabricated with optimized ZnS/Ag/ZnS coatings as transparent conductors. The use of multilayer ZnS/Ag/ZnS film was found to improve the electrical characteristics and to lower the emittance of the devices.

A dielectric layer produces an antireflection effect when deposited on the side of light incidence on the metal, and thus serves to increase the transmittance [11]. The metallic film can also be embedded between two anti-reflection dielectric layers [12]. Such a three-layer structure allows broadband reflectance and flexibility in band pass selection [13]. The main criterion for the selection of the dielectric, for a given metal, is that the refractive index of the dielectric should match substantially the extinction coefficient of the metal in the desired spectral range [14]. 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. D/M/D layers on glass substrates, e.g., TiO$_2$-Ag-TiO$_2$ [15], ZnS-Ag (or Al)-ZnS [16], and WO$_3$-Ag-WO$_3$ [17] have been used to fabricate heat mirrors that are energy efficient for cold or hot climates.

In recent years nanocrystalline ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counterparts. Zinc Sulphide is a dielectric potentially important material to be used as an antireflection coating for heterojunction solar cells, [18]. Therefore much effort has been made to control the size, morphology and crystallinity of ZnS thin film. However, there has been growing interest in developing techniques for preparing semiconductor nano particles and films. Several techniques have been employed to prepare ZnS thin films such as Physical vapor deposition, (Thermal, electron beam and sputtering Atomic layer depositions) [19]. Spray pyrolysis [20], Molecular beam epitaxy [21], RF reactive sputtering [22].

Heat mirror coatings may be deposited on plastic or glass substrates using differing deposition processes depending on the materials used. Two basic materials systems are used. Multilayer coatings utilize a metallic layer (such as copper, silver or gold) reflective to the infrared and one or more dielectric layers as antireflection layers to improve visible transmittance and increase durability. Single layer of some semiconductors (such as, ZnS, WO$_3$, TiO$_2$) is intrinsic transmitters of short-wave energy but are reflective to long-wave infrared.

Semiconductor type heat mirrors have been produced primarily by high-temperature pyrolysis processes which has restricted their use to glass substrates, although some can also be produced at lower substrate temperatures using a sputtering process. The selection of materials and production process has an important impact on ultimate product cost as well as influencing factors such as performance and durability [23].

The performance of an ideal transparent heat mirror is shown in Figure 1. For passive solar application, the transmission window should extend from 0.3 μm to approximately 2.5 μm wavelength, while for other applications where illumination is important but heat gain may not be, the transmission window need only extends to 0.7 μm. The coating should exhibit high reflectivity to long-wave infrared from approximately 5-20 μm.

![Figure 1. Desirable heat mirror properties](image)

The aim of this project is to introduce a mechanism to fabricate heat mirrors that are energy efficient. Heat mirrors were fabricated by depositing multilayer ZnS-Ag-ZnS on glass substrates. In all films the degree of crystallinity, crystal structure and roughness over raid the optical properties. It is common knowledge that the films produced by different processes, or indeed, in different deposition systems have different optical constants. Moreover, by varying the material and thicknesses of the three layers, the optical properties of the dielectric-metal-dielectric films can be tailored to suit different applications. Therefore, optical properties of single films were measured, and a computer code for an optimization of the performance of the heat mirror was developed.

II. EXPERIMENT

Glass substrates were cleaned sequentially by ultrasonication in acetone and deionized water for 10 min. Then the substrates were dried in a high purity N$_2$ gas stream just before loaded with substance (ZnS) into the vacuum chamber. High purity (99.99%) polycrystalline ZnS was selected as source. Further, the substrates were subjected about 5 min to glow discharge cleaning before deposition. Nanostructure thin films of ZnS were deposited on a glass substrate at different substrate temperatures (20 °C, 100 °C and 150 °C) by electron beam evaporation. The vacuum system employed in this research was “Edwards AUTO 306, Sputtering System” The substrate fixed in the sample holder and the ZnS filled in the graphite boat. Then the system was ready to operate and evacuated. Chamber pressure was below 3x10$^{-6}$ Torr. The evaporation rate of ZnS was around 0.1 nm.s$^{-1}$. The thickness of the layers was measured in the range 40-50 nm using a quartz crystal thickness monitor. The thickness was calibrated by spectroscopic ellipsometry (SE) model SENTECH in the range 190-1100nm and at the incident angles of 50, 60, and 70 degrees.
Imaginary and real part of the refractive index \((n=\varepsilon_r+ik)\) measured by SE. The film structural analysis was accomplished by XRD “Philips X-ray diffraction system with the setting of, (40 kV, 30 mA, CuKa wavelength of 1.540598 Å in the scan range of 2θ between 10° and 80° with 0.05 (2θ s\(^{-1}\)) step size”.

### III. RESULTS AND DISCUSSION

ZnS has two crystal structures so is an allotropy/polymorphism compound. Allotropism is a behavior exhibited by certain chemical elements that can exist in two or more different forms, known as allotropes of that element. In each allotrope, the element’s atoms are bonded together in a different manner.

XRD patterns of ZnS thin film deposited at 20, 60 and 100 °C shown in Figure 2. Sample 1 (room temperature, 20 °C) displays two low intensity peaks that refer to both Wurtzite and Zinc blend structures of ZnS. In sample 2 (temperature of 60 °C) there are 3 sensible peaks. These peaks are stronger and wider. Concluded that, sample 2 has series polycrystalline plans with diminutive particles. Sample 3 (temperature of 100 °C) no crystalline structure on the scale of other spectra was observed. So, XRD patterns induce that sample 2 favorite for further study.

![XRD patterns of ZnS films 1, 2 and 3 deposited at (20 °C), (60 °C) and (100 °C) substrate temperature, respectively.](image)

In order to determine real thicknesses of layers and optical parameters ellipsometry spectroscopy for the selected samples 1 and 3 were done one roughness is high the other with large grains. Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured values are ellipsometric parameters, delta and psi. These values are related to the ratio of reflection coefficients \(r_p\) and \(r_s\) for p and s polarized light as follows:

\[
\rho = \frac{r_p}{r_s} = \tan(\delta) \exp(i\Delta)
\]

where \(\rho\) is the ratio of reflection coefficients and \(i\) is the imaginary unit. In case of thin film layers, information of the thicknesses is included in \(\Delta\) and \(\Delta\) and the thickness of each layer can be determined by best fitting between the experimental data and calculated data by usual thin film optics calculations [24].

The EMA and Cauchy imaginary models used for rough and main ZnS layers respectively. The Cauchy parameterization is a mathematical fit which is only applicable in frequency ranges of the spectrum where the extinction coefficient is zero. In regions where there is no absorption the Cauchy model provides a sufficient description of the dielectric function.

One main advantage of its use is in the low number of free parameters. The Cauchy model is represented as in equation 2 and 3 [25].

\[
n(\lambda) = A_1 + \frac{B_1}{\lambda^2} + \frac{C_n}{\lambda^3}
\]

\[
k(\lambda) = A_2 e^{\left(\frac{h}{\lambda}\right)-C_1}
\]

where \(A, B, C\) and \(h\) are constant. If the use of the Cauchy model is taking place in the spectroscopic region with no absorption, \(k\) is simply 0 and the model reduces to three fit parameters. This is particularly useful when using ellipsometry to simply fit for thickness.

Additionally, interfacial regions between layers can exist which are not simply one or another material type, but rather a percent of one and a percent of the other. This type of layer is different from an alloy, in that material \(A\) and \(B\) are not uniformly distributed throughout the thickness. This kind of layering is represented by an effective medium approximation or (EMA). EMA models normally use to describe the microscopic surface roughness, [26]. In general, EMA layers will be described by a certain thickness, a shape factor, and ratio of material \(A\) to \(B\). EMAs are also useful in describing porous materials, or materials which have a certain void percentage distributed throughout [27]. The EMA used to describe surface roughness layers in this work is the Bruggeman EMA to work well with perovskite films, [28] these models are shown in Figure 3.

![Thickness and optical parameters of samples 1 (up) and 3 (down)](image)
wavelength variation. Refractive index varies with the wavelength of the incident light according to Sellmeier equation. The Sellmeier equation (an equation for calculating the wavelength-dependent refractive index), [29] is an empirical relationship is used to determine the dispersion of light in the medium.

Table 1. Calculated and measured parameters and properties of samples

<table>
<thead>
<tr>
<th>Sample Parameters</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>20 °C</td>
<td>60 °C</td>
<td>100 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>Thickness of monitor</td>
<td>15 nm</td>
<td>15 nm</td>
<td>15 nm</td>
<td>15 nm</td>
</tr>
<tr>
<td>Thickness of ellipsometry</td>
<td>35.3 nm</td>
<td>-----</td>
<td>38.4 nm</td>
<td>-----</td>
</tr>
<tr>
<td>Percent of void (capillary)</td>
<td>2%</td>
<td>-----</td>
<td>50%</td>
<td>-----</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.76</td>
<td>-----</td>
<td>2.48</td>
<td>-----</td>
</tr>
<tr>
<td>Thickness of rough layer</td>
<td>6.02 nm</td>
<td>-----</td>
<td>14.1 nm</td>
<td>-----</td>
</tr>
<tr>
<td>RMS Roughness</td>
<td>0.6 nm</td>
<td>-----</td>
<td>11.2 nm</td>
<td>-----</td>
</tr>
</tbody>
</table>

Table 2. Statistical parameters of samples 1, 2, 3, respectively

<table>
<thead>
<tr>
<th>Roughness result</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS roughness</td>
<td>0.6238</td>
<td>0.6083</td>
<td>10.1521</td>
</tr>
<tr>
<td>Peak to peak</td>
<td>6.2018</td>
<td>5.6248</td>
<td>88.3702</td>
</tr>
<tr>
<td>Roughness average</td>
<td>0.4761</td>
<td>0.4733</td>
<td>7.9125</td>
</tr>
<tr>
<td>Average height</td>
<td>2.3015</td>
<td>2.9001</td>
<td>28.005</td>
</tr>
</tbody>
</table>

The usual form of the equation for glasses is

\[ n^2(\lambda) = A + \frac{B\lambda^2}{\lambda^2 - C} \]  \hspace{1cm} (4)

where, \( A, B \) and \( C \) are constant. If all terms are specified for a material, at long wavelengths far from the absorption peaks the value of \( n \) tends to

\[ n^2 = \varepsilon \]  \hspace{1cm} (5)

where \( \varepsilon \) is the relative dielectric constant of the medium.

Dielectric layers have a precious relation (Cauchy relation) near to a polynomial for a certain spectral range (Equation (6)):

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]  \hspace{1cm} (6)

As previously mentioned, in SE the values of \( A, B \) and \( C \) are constant and calculated for layer and refractive indices are given by wavelength. Figure 4 shows the refractive index of sample 1 and 2 in the wavelength range of 250 nm to 850 nm.

Figure 5 shows the refractive index of ZnS thin film for three thicknesses (100, 200, 400 nm). According to the figure refractive index was increased with increasing the thickness due to grain size variation.

The presence of big valleys in the film, more prominent in the rough layer of thin films gave rise to the mean refractive index lower that for bulk material. A change in the refractive index of ZnS films which was confirmed to be due to the temperature rise resulting from the absorption of incident light.

IV. CONCLUSIONS

This paper examines some of the issues relating to utilization of transparent heat mirrors for energy conservation and passive solar heating purposes. The reduction of heat transfer rates by the use of thermal infrared reflecting materials has been practiced in both architectural and on-architectural applications for many years nevertheless, far from an ideal conclusion. It appears that cost-efficient coatings promising savings of 25-75%, depending upon application, may be available to window manufacturers and homeowners in the near future. Performance, applications and limitations are considered. zinc sulfide 40 nm thin film was deposited by electron beam vapor deposition technique. The effect of substrate temperature on crystal and optical properties of ZnS thin films were considered. The grain size of films deposited at a substrate temperature of 60 °C was small as compared to the films prepared at other substrate temperatures. By increasing the temperature, from 60 °C to 150 °C, RMS roughness increase from 0.6 nm to 11.57 nm. SE analyses indicate increase the thickness of the rough layer with increasing the temperature. The refractive index of ZnS thin film was lower than those for bulk ZnS. This is because of voids, more marked in the thinner film.

NOMENCLATURES

RMS roughness: Root Mean Square Roughness
D/M/D: Dielectric/Metal/Dielectric
EMA: Effective Medium Approximation
SE: Spectroscopic Ellipsometry
\( n \): Refractive index
\( k \): Extinction coefficient
\( \lambda \): Wavelength
\( \varepsilon \): Relative dielectric constant
\( r_p \): Reflection coefficient for parallel polarized light
\( r_s \): Reflection coefficient for perpendicular polarized light
BIOGRAPHIES

Ghassem Kavei received his B.Sc. in Applied Physics from University of Tabriz, Tabriz, Iran, M.Sc. degree in Atomic Physics from the Southampton University, UK and his Ph.D. in Surface Physics from Keele University, UK. He is a member of Iranian Crystallography Association (ICA) and Iranian Physics Society (IPS). He has co-authored approximately 11 books, and has published over 65 publications on various aspects of atomic physics, thermoelectric, TiO2 thin film, SPM application, ITO thin film and nano-science and technology. He was also a lecturer at several universities in Iran teaching different subject in electron physics. Currently, he is a Research Professor at the Material and Energy Research Centre, Tehran, Iran and applied for a permission to publish a periodical scientific International Journal “International Materials Physics Journal”.

Saeed Nikbin was born in Mashhad, Iran, 1987. He received the B.Sc. degree from University of Mazandaran, Babolsar, Iran. Currently, he is studying his M.Sc. on Nanotechnology in Material and Energy Research Center, Tehran, Iran. His research interests are in the area of optical properties of thin films and renewable energy.