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Thermal Treatment Effect of Manganese Sulfide (MnS) Thin Films

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Abstract: ***Thin-films of Manganese Sulfide (MnS) were prepared by thermal evaporation method, on glass substrate which has thickness of 1mm, and refractive index 1.52 under high vacuum of 2×10^{-7}torr. Differential Thermal Analysis (DTA) for MnS in powder form revealed that melting point is 700C^o. The effects of thermal treatment beside the transmission of MnS were investigated. After heat treatment is found that the light transmission is temperature dependent in the visible and ultraviolet-visible region. The optical properties, like absorption coefficient, transmission were calculated for each sample.***

Keywords: MnS, Thin-films, Differential Thermal Analysis (DTA), absorption coefficient, transmission, Physical vapor deposition PVD

1. Introduction

The study of thin films is very large interesting subject for its wide applications. it used for many applications such as mirror surfaces, Manganese sulfide (MnS) is important compound of amorphous semiconductors, it is a wide band gap (Eg = 3.1 eV) semiconductor with potential interest in short-wavelength optoelectronic applications such as in solar selective coatings, solar cells, photoconductors, optical mass memories and dilute magnetic semiconductor [1, 2].

The aim of this study is to investigate, the effects of thermal treatment of MnS thin films and its optical properties which substrates by Physical Vapor deposition, beside the Characterization (Transmission and Absorption) of MnS thin films. Preparation of MnS has been carried out by different methods such as, thermal evaporation and other methods [3, 4].

The optical properties of manganese sulfide films, were deposited by the physical vapor deposition technique. The optical constants of the film were determined from Spectrophotometric measurements of transmittance.

This study is based on analytical and experimental technique to determine the optical properties of MnS,optical radiation lies between radio waves and x-rays on the spectrum, The surprising dual nature of light is a couple, one nature is (electromagnetic) wave and the other nature is particles [5,6, 7].

The wave nature of light is described by the Maxwell's electromagnetic plane wave equations:

$$\nabla^2 \mathrm{E} = (1/\mathrm{v}^2)\left(\frac{\eta \mathrm{E}}{\mathrm{t}^2}\right) ,$$

$$\nabla^2 \mathrm{H} = (1/\mathrm{v}^2)\left(\frac{\eta \mathrm{H}}{\mathrm{t}^2}\right) \quad (1\text{-}1)$$

$$\nabla \mathrm{D} = \rho \quad , \quad \nabla \mathrm{B} = 0 \quad (1\text{-}2)$$

Where ∇ is the Laplacian operator, v is speed of wave in a medium, E and H are the electric and magnetic fields, respectively, D is the electric displacement vector (its gradient is the charge density p), and B is the magnetic induction vector. These four vectors are interrelated as:

$$\mathrm{D} = \varepsilon_0 \mathrm{E} + \rho \, , \, \mathrm{B} = \mu_0 \mathrm{H}_0 + \mathrm{M} \quad (1\text{-}3)$$

Where ε_0 and μ_0 are the dielectric permittivity and permeability, respectively, both constants of free space, P and M are the electric polarization and the magnetic polarization of the wave, respectively.

When an electromagnetic wave propagates in a linear (e.g., noncrystalline) medium, the electric polarization is expressed as,

$$\rho = \varepsilon_0 \chi \mathrm{E} \quad (1\text{-}4)$$

Where χ is the electric susceptibility of the medium (in a nonlinear medium, this is expressed as a tensor), the dielectric constant of the material, ε, is connected with the susceptibility as

$$\varepsilon = \varepsilon_0 (1 + \chi) \quad (1\text{-}5)$$

the smallest quantity of monochromatic light, described by the energy equation:

$$E = \mathrm{h}\upsilon \qquad , E = hc/\lambda \quad (1\text{-}6)$$

υ is the frequency of light. Visible light consists of continuum of wave lengths that span (visible) spectrum from deep red 700nm to deep violet-blue 400nm [5,8].

Absorbance is the fraction of the incident flux that is absorbed. An absorption coefficient (α) in (cm^{-1}) is often used in the expression.

$$\tau_i = e^{-\alpha x} \quad (1\text{-}7)$$

Where τiis internal transmittance and (x) is path length (cm).

In most cases, absorbance is not directly measured, but is interfered from transmission measurement, with appropriate correction for reflection losses. These corrections can be calculated from the Fresnel equation if the surfaces are polished and the index of reflection is known. For materials where the absorption is extremely small, this method is unsatisfactory, as the uncertainties are dominated by the reflection contribution [10].

In linear optics the incremental decrease of the intensity I, when absorption coefficient (α) measured in cm^{-1}:

$$I = I_o e^{(-\alpha x)}\ , \quad A = \log\frac{I}{I_o} \qquad (1\text{-}8)$$

$$and\ \alpha = (h\upsilon - Eg)^{\frac{1}{2}}\ , \quad \alpha = \frac{1}{x}Ln(T) \qquad (1\text{-}9)$$

The transmission or transmittance

$$T = \frac{I}{I_o}\mathrm{T} \qquad (1\text{-}10)$$

It can be shown that for absorption or emission of phonons, the material has to perform a transition between two eigen-states E_m and E_p of the material and thus the photon energy has to fulfill the resonance condition as below:

$$E_{photon} = h\upsilon_{photon} = (E_p - E_m)E_{photon} \qquad (1\text{-}11)$$

Spectral emitance ε (λ) is the emittance at a given wavelength, If a radiance is natural with respect to wavelength, with a constant spectral emittance less than unity, it is called a gray-body.

$$\varepsilon = \frac{L}{L^{bb}}\ , \qquad \varepsilon(\lambda) = \frac{L_\lambda}{L\lambda^{bb}} \qquad (1\text{-}12)$$

Where: L is radiance of object or surface. And L^{bb} is radiance of black body. If the body is non–gray, its emittance is dependent upon temperature in as much as the integral must be weighted by the source (Planck) function[10].

The relation between transmittance, reflectance, and absorbance:Radiant flux incident upon surface or medium undergoes transmission, reflection, and absorption. Application of conservation of the energy leads to the statement that the sum of the transmission, reflection and absorption of the incident flux is equal to unity, or:

$$\alpha + \tau + \rho = 1 \qquad (1\text{-}13)$$

In the absence of nonlinear effects

$$\alpha(\lambda) + \tau(\lambda) + \rho(\lambda) = 1 \qquad (1\text{-}14)$$

If the situation is such that one of the above relations is applicable, then emittanceεmay be substituted for absoptance (α) in the previous equations [9].

$$\varepsilon = 1 - \tau - \rho, \varepsilon(\lambda) = 1 - \tau(\lambda) - \rho(\lambda) \qquad (1\text{-}15)$$

There is considerable number of processes that can be used for the deposition of optical coatings. The comments take place under vacuum and can be classified as physical vapor deposition (PVD) and chemical vapor deposition (CVD).

Today high temperature of CVD processes for producing thin films and coating have found increasing application in such diverse technologies as the fabrication of ball bearing and cutting tools , the production of rocket engines and nuclear reactor components. In thin film technology research's interested in deposition of thin film and thin film structure [11, 12].

Thermal evaporation is one of the most famous two physical methods of preparation of thin films; it is more widely known and used , A vast number of material can evaporated in vacuum and be caused condense on surfaces. Most of these materials can be sublimed, for example magnesium, cadmium, Zinc sulfide.In evaporation processes describe evaporation rate (flux) from kinetic theory for evaporation, the vapor pressure is:

$$P_{evaporation} = 3\times 10^{12}\sigma^{\frac{3}{2}}T^{\frac{1}{2}}e^{\left(\frac{\Delta H}{nKT}\right)} \approx P_o^{\left(\frac{E\alpha}{KT}\right)} \qquad (1\text{-}16)$$

Where σ is the surface tension of the liquid, n is Avogadro's number , T is absolute temperature, And$\Delta H$is the enthalpy of evaporation.

To define the number of molecules crossing a plane per unit time as:

$$J = \sqrt{\frac{P^2}{2\pi KTm}} \qquad (1\text{-}17)$$

Where P is pressure in Pascal's, K is Boltezmann constant, T is absolute temperature, and m is the atomic or molecular mass.

If the liquid is assumed to be a constant temperature and the deposition rate is:

$$R_d = \sqrt{\frac{P^2}{2\pi KTm}}\cdot\frac{P_{evaporation}}{\sqrt{T}}\cdot\frac{Area}{4\pi r^2} \qquad (1\text{-}18)$$

Where ρ is the mass density (kg/m^2). Area is the area of the wafer, And r is the radius of the sphere.

Sputtering is a technology in which the material is related from the source at much lower temperature than evaporation. The substrate is placed in a vacuum chamber with the source material, named a target, and an inert gas (such argon) is introduced at low pressure, the type source in these technology including DC sputtering and magnetron sputtering [14].

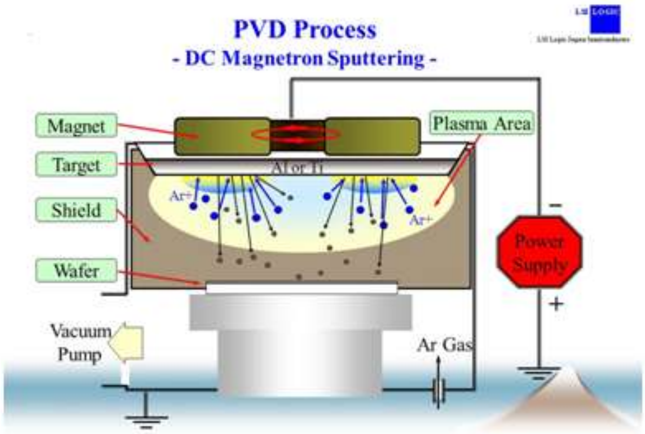

Figure 1: Magnetron sputtering process.

Optical properties of thin films: The wave length dispersion instruments for (0.185- to8.00) μm spectral range is usually provided by prisms or by ruled or holographic gratings. Grazing incidence gratings, crystal, or multilayer coatings are used in the soft x-ray and extreme ultraviolet (XUV) spectral regions.The transmittance, reflectance, and absorbance of some optical coatings are affected by exposure to atomic oxygen and by electron, proton, and ultraviolet irradiation [13, 15]. Thin films usually used for example in coating the glass and lens, improve the property of material and for decoration. Thin film applications requiring electron beam evaporation, its continually increasing. Applications are found in the medical, metallurgical, telecommunication, microelectronic, optical coating nanotechnology, and semiconductor industries [11]

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2. Sample Preparation

Different samples were prepared from Manganese Sulfide under different temperatures forum 50 to 200Co in Pressure 2×10^{-7} $torr$with variation times (30& 45 minute).

3. Results and Analysis

Manganese Sulfide thin films were deposited on glass substrate that have refractive index 1.52 and thickness (1 mm) , the transmission , reflection and absorption coefficient were measured by using Beers-Lambert law, the data of optical properties the samples were recorded.

4. Discussion

The results of differential thermal analysis (DTA) for manganese Sulfide powder are depicted in figure below. The melting point of MnS is 700 C^{o}, the first exothermic peak at 112.14C^{o}it,s a result of crystalline grain growth.The last endothermic peak 356.31C^{o}it,s a result Mns polychromic transformation.

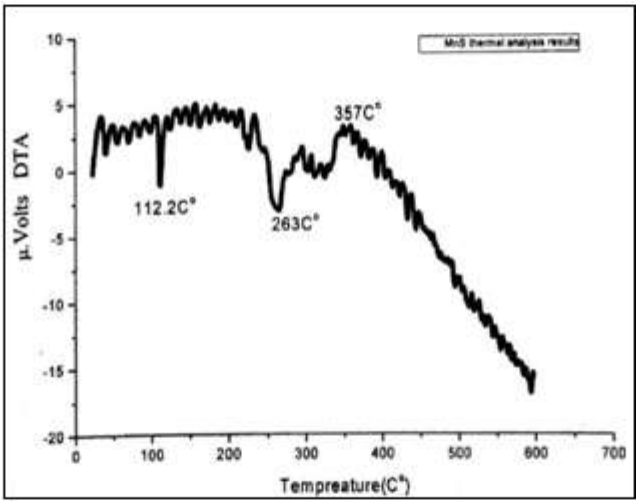

Figure 2: diagram of as synthesized MnS powder form.

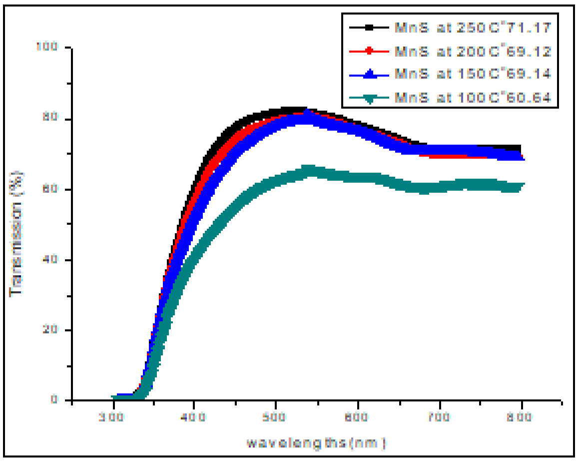

Figure 3: Show that transmission spectrum of MnS versus wave lengths

In the region between 307 to 577 nm, it's clear that the transmission (%) for MnS sample at 577nm is very high compared with others wave lengths. This is a good indicator to use this material in property to produce an optical filter and band transmitter at this wave length.

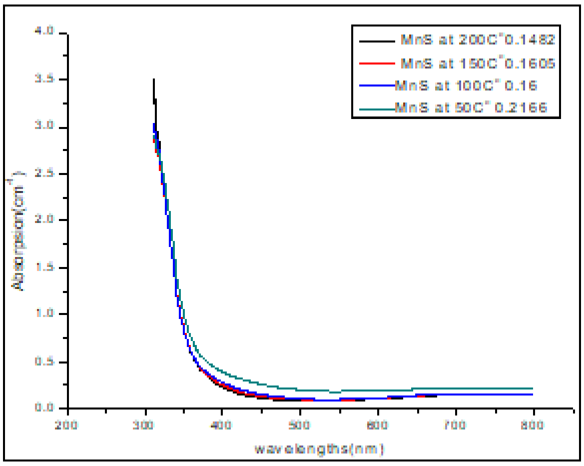

Figure 4: Absorption spectrum of MnS

This figure can deduce that the absorption is maximums for the wave lengths, in the wavelength 400 to 800nm. Thus such sample can be utilized as solar heater or solar cell.

5. Conclusion

The light transmission is temperature dependent in the visible and ultra violet – visible region.At high temperature the layer showed thermal instability.The optical properties like transmission indicate that, the films can be utilized as band pass or filters, to some lengths.

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