UNIVERSITI PUTRA MALAYSIA

EFFECT OF AGING AND HEAT TREATMENT ON THE OPTICAL PROPERTIES OF ZnS, SnS AND Se THIN FILMS

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Chairman : Associate Professor Dr. Hj. W. Mahmood Mat Yunus, Ph.D.

Faculty : Science and Environmental

Study on the optical properties of ZnS, SnS and Se thin films in polycrystalline and amorphous structure was carried out at room temperature. Double beam UV-spectrophotometer was used to obtain the transmissions curve. The measurement of transmission for each sample was conducted in the range of 300 to 1100 nm, and the structures of samples were analyzed using X-ray diffraction spectrometer. Swanepoel (1983) method had been used in this study to determine the optical properties of the ZnS, SnS and Se thin films.

Data from theoretical calculation was also used to cross-check the validity of the optical data of the samples. The results show that the refractive index of the samples decreases as wavelength increases. The energy band gaps of the samples are in good agreement with the data reported in the literature previously. The results also show that the refractive index of the samples is thickness dependent. However, the energy band

gaps for all the samples were found to be independent of film thickness in the range of 370 up to 742 nm. While the energy band gaps of the Se thin films decreases with increasing film thickness.

Three procedures of measurement were investigated for the samples. First, measurements were done immediately on the samples after they were deposited. Second, the measurement of the samples was done after they were exposed to the air. Third, the effect of annealing at different times in addition to different temperatures in ranging from (40 - 120) °C in ambient atmospheric pressure was studied. The results indicated that, the refractive index decreased with increasing the wavelength in all cases.

Other results in the present study indicate that the aging have more significant effect on the refractive index, plasma energy and energy band gap of the ZnS and Se samples. Furthermore the refractive index and the energy band gap of the a-ZnS were not affected with the annealing time, while the energy band gap of the SnS was affected with annealing temperature.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

KESAN PEAUAAN DAN HABA KE ATAS SIFAT OPTIK FILEM NIPIS ZnS, SnS dan Se.

Oleh

ABUBAKER EL SHEIKH ABD EL RAHMAN

Disember 2000

Pengerusi : Profesor Madya Dr. Hj. W. Mahmood Mat Yunus, Ph.D.

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Kajian sifat optik filem nipis ZnS, SnS dan Se dalam bentuk struktur polihablur dan amorfosnya telah dilakukan pada suhu bilik. UV-spektrofotometer dua-alur digunakan untuk memperolehi taburan spektrum transmisi. Pengukuran ke atas filem-filem nipis ini dibuat dalam julat jarak gelombang 300 hingga 1100 nm. Struktur filem-filem ini pula dikaji dengan menggunakan spektrometer pembiasan sinar-X. Kaedah Swanepoel (1983) telah digunakan dalam kajian ini untuk menentukan sifat optik bagi filem-filem nipis ZnS, SnS dan Se.

Pengiraan juga telah dibuat untuk menguji ketepatan data yang diperolehi. Keputusan menunjukkan bahawa indek pembiasan filem-filem berkurang apabila jarak gelombang bertambah. Data jalur tenaga terlarang yang diperolehi amat menyetujui dengan nilai yang telah dilaporkan oleh penyelidik-penyelidik lain. Keputusan juga menunjukkan bahawa nilai indek pembiasan bergantung kepada ketebalan sampel. Akan tetapi, tenaga jalur bagi filem-filem ini didapati tidak bergantung kepada ketebalan

sampel sehingga 742 nm. Bagi ketebalan sampel Se yang melebihi 742 nm, tenaga jalur terlarang berkurang dengan penambahan ketebalan sampel.

Tiga langkah pengukuran telah dilakukan untuk mengkaji filem-filem ini iaitu pertama, pengukuran dibuat sebaik sahaja siap disediakan. Kedua, pengukuran dibuat selepas filem-filem terdedah kepada udara. Ketiga, mengkaji kesan pemanasan pada tekanan atomosfera tetapi pada masa dan suhu (40 - 120) °C yang berlainan. Keputusan menunjukkan bahawa nilai indeks biasan berkurang dengan peningkatan jarak gelombang.

Hasil keputusan yang lain menunjukkan bahawa kesan penuaan memberikan kesan yang lebih ketara pada indeks biasan, tenaga plasma dan tenaga jalur. Nilai indek biasan dan tenaga jalur pada sampel ZnS dan Se. Tambahan pula, indeks biasan dan tenaga jalur terlarang bagi a-ZnS menunjukkan ia tidak dipengauhi oleh masa pemanasan, manakala tenaga jalur bagi SnS dipengauhi oleh suhu pemanasan.

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LIST OF SYMBOLS

a-ZnS	Amorphous Zinc Sulfide
c-ZnS	Polycrystalline Zinc Sulfide
a-Se	Amorphous Selenium
T	Transmission of the Film
T %	Transmission of the Film (percentage)
T_u %	Experimental Data of Transmission (percentage)
R_1%	Reflection of Film-air Interface (percentage)
R_2 %	Reflection of Film-substrate Interface (percentage)
R_3 %	Reflection of Substrate-air Interface (percentage)
T_s%	Transmission of Glass Substrate (percentage)
d	Film Thickness
d_{true}	True Film Thickness
T_M	Maximum Transmission
T_m	Minimum Transmission
T_a	Interference Free Transmission
n	Refractive Index of film
n_{true}	True Refractive Index of Film

N^*	Complex of Refractive Index
s	Refractive Index of Substrate
n_o	Refractive Index of Air
λ	Wavelength (nm)
K	Wave Vector
$h\nu$	Photon Energy (eV)
α	Absorption Coefficient (cm^{-1})
δ	Integer Number
m	Number of Fringes
E_g	Energy Band Gap of the Film (eV)
E_o	Average Oscillator Energy (eV)
E_d	Dispersion Energy (eV)
E_p	Plasma Energy (eV)

CHAPTER I

INTRODUCTION

The optical properties of the material are related to the characteristics of the electromagnetic wave absorption and emission. The optical properties are also play an important role in developing and understanding of the structural and electronic properties of semiconductors thin film. Nevertheless, the optical properties of thin film could be found from the amplitude and state of polarization of a light beam, in the form of the Fresnel coefficient of reflection and transmission.

This study focuses on optical properties of Zinc sulfide (ZnS), Tin sulfide (SnS) and selenium (Se) semiconductor in thin film form. These materials attract much attention at different phase due to various physical applications.

Zinc sulfide is currently used in flat-screen solid state displays and can be employed in the new generation of visible light emitting laser diode. High durability ZnS found useful in harsh commercial and military environment (Carl and Francis 1980). Studies on X-ray photoelectron spectroscopy by Olga *et al.* (1997), found that ZnS formed adherent film to glass substrate. The adherent process was further developed to produce the metal sulfide thin film photographic. However, ZnS compound was found to exhibit insulating behavior as well. This phenomenon could be due to an increase in the metallic component of binding and a decrease in the ionic component (Abrikosov *et al.* 1969).

According to Mishra *et al.* (1989) and Zulkarnain *et al.* (1997), even though SnS compound is relatively less studied, it is a promising material for the production of low cost material for solar energy conversion. The phase diagram of the SnS formed monochalcogenides in addition to more complex compounds comprised mainly of SnS_2, Sn_2S_3 and Sn_3S_4 compositions, depending on the temperature and percentage of the constituents. Also SnS and SnS_2 were found to be the most stable compound with regard to melting points of (855 ± 5) °C for the case of the sulfur atoms between 10 - 48 % and 68 - 95 % respectively (Abrikosov *et al.* 1969).

Selenium is widely used in commercial applications for example xerography and image processing. Zishan *et al.* (1997) stated that pure selenium has short lifetime, however Kotkata and Abdel Wahab (1990) observed that light could enhanced the crystallization process of the amorphous Se, at low temperature. They also established that the increase of the crystal growth rate by light heating could be resulted from the reproduction of hole-electron pairs in the amorphous Se thin film.

Objective

The aim of this study is to characterize the optical properties of ZnS, SnS and Se thin films. Double beam UV-spectrophotometer was used in this study to measure the transmission spectra. Also as the transmission curve for each sample was determined, the samples were considered homogenous and isotropic with uniform thickness. Studies on optical properties are limited to optical constants, plasma energy and band gap energy. The analyses were carried out based on transmission spectra. Therefore, the objectives of the present study were:

1 - To characterize the optical properties of ZnS, SnS, and Se thin films.

2 - To study aging effect and heat treatment on the optical properties of ZnS, SnS, and Se thin films.

Thin film

Thin film material can be either of crystalline or amorphous structures. A single crystal structure contains atoms that arranged in periodic arrays. Polycrystalline material consists of a matrix of crystallites, each crystal is essentially a single crystal with a different crystal axis orientation to its neighbor. It gives rise to the periodic potential within which the electrons exist. On other hand amorphous materials contain conveniently bonded atoms, which are arranged in an open network. The bonded atoms correlate with each other in order up to the third or fourth nearest neighbors. The short-range order is directly responsible for measurable semiconductor properties, such as optical and electrical.

Optical Constants

The theoretical and experimental investigations on the optical behavior of thin films deal primarily with optical constants. The optical properties of the amorphous and crystalline semiconductor materials can be described by complex refraction index, $N^* = n - ik$. The real and imaginary parts of N^* are termed as refractive index and absorption index. The n and k are referred to as the optical constants of the medium. Generally, the optical constants are photon energy dependent and exhibit in interband regions, where the electron transitions are dominant. The bound electrons, which are present in semiconductor compounds, can be described in terms of complex dielectric constant, as $N^{*2} = \varepsilon_1 - i\varepsilon_2$, were ε_1 and ε_2, are the real and imaginary parts of dielectric.

The Energy Band Gap

Optical thin film theory is based on the Maxwell macroscopic theory of electromagnetic waves, as applied to the propagation of light across the thin films. The basic electronic band is mainly concerned with excitation of electrons above the band gap. In this process, holes are left behind in the valence band. The electrons and the holes can be treated as charged quasi-particles that move through periodic lattice with an effective mass. According to Nasser *et al.* (1993) the band gap of semiconductor gives a best understanding of fundamental electronic structure of solid, and can determine whether the band gap is a direct or an indirect allowed transition. The measurements of the optical band gap can be done in a simplest way by measuring the absorption edge. Generally, in the various absorption processes, the electrons and holes absorb both photons and phonons. The photons supply the required energy, while the phonons supply the required momentum. In such a situation, the lowest threshold of the band gap energy cannot be achieved for a process that involves only photon energy. However, in the direct transition, the photon-initiated transitions require a constant wave vector, k. On the other hand the indirect allowed transition in which the k vectors of initial and final states are different; the phonon-assisted transition can still conserve momentum.

Direct and Indirect Band Gap Semiconductors

Semiconductor material can be divided into two main transition groups, namely direct and indirect gaps. When the vertical transitions between valence and conduction band are allowed, and the photons are only involved in this transition, the material is called direct band gap semiconductor. The direct transition occurred in ZnS, CdS, GaAs and InSb and many more compound III - V or II - V materials. On the other hand, when the transitions between the valence band and conduction band are not linear and the transition is associated with photon-phonon coupling, the materials are called indirect band gap semiconductors. This type is found in Si, Se, SnS and Ga semiconductor materials. This phenomenon is displayed in Figure 1.1.