



Influence of deposition time on the properties of chemical bath deposited manganese sulfide thin films

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Resumen

Películas delgadas de sulfuro de manganeso fueron depositadas químicamente a partir de soluciones acuosas que contenían sulfato de manganeso, tiosulfato de sodio y tartrato de sodio. Se investigó la influencia del tiempo de deposición (2, 3, 6 y 8 días) sobre las propiedades de las películas. La estructura y morfología de las películas fue estudiada empleando difracción de rayos X (DRX) y microscopía de fuerza atómica (MFA). Adicionalmente, a objeto de estudiar las propiedades ópticas de las películas se empleó la espectroscopia UV-visible. Los resultados de la DRX indicaron que las películas de MnS_2 depositadas poseen una estructura cúbica policristalina. El número de picos observados en el patrón de la DRX se incrementa de tres a seis y luego disminuye a cinco, a medida que el tiempo de deposición aumentaba de 2 a 8 días. A partir de los estudios de MFA, se encontró que el grosor y la rugosidad de las películas de MnS_2 dependen del tiempo de deposición.

Palabras clave: Propiedades ópticas; Sulfuro de manganeso; Películas delgadas; Difracción de rayos-X

Abstract

Manganese sulfide thin films were chemically deposited from an aqueous solution containing manganese sulfate, sodium thiosulfate and sodium tartrate. The influence of deposition time (2, 3, 6 and 8 days) on the properties of thin films was investigated. The structure and surface morphology of the thin films were studied by X-ray diffraction and atomic force microscopy, respectively. In addition, in order to investigate the optical properties of the thin films, the UV-visible spectrophotometry was used. The XRD results indicated that the deposited MnS_2 thin films exhibited a polycrystalline cubic structure. The number of MnS_2 peaks on the XRD patterns initially increased from three to six peaks and then decreased to five peaks, as the deposition time was increased from 2 to 8 days. From the AFM measurements, the film thickness and surface roughness were found to be dependent on the deposition time.

Keywords: Optical properties; Manganese sulfide; Thin films; X-ray diffraction.

Introduction

Manganese sulfide is an important semiconductor material because of its interesting properties, such as direct band gap, abundance in nature and absence of toxicity. Thus, manganese sulfide thin films have been widely used in a variety of applications such as solar cells¹, solar selective coatings, sensors, photoconductors², optical mass memories and antireflection coating³. Several methods have been applied to obtain manganese sulfide thin films such as radio-frequency sputtering⁴, hydrothermal⁵, SILAR⁶ and chemical bath deposition^{1,7}. Chemical bath deposition technique is simple, low cost and convenient for large area deposition of films. In chemical bath deposition method,

controlled chemical reaction plays a key role for the deposition of the thin films. The substrates are immersed in solution containing the chalcogenide source, the metal ion and a complexing agent. The preparation of various thin films using chemical bath deposition method such as ZnS^8 , CdS^9 , CuS^{10} , $CdS_{1-x}Se_x^{11}$, $Pb_{1-x}Fe_xS^{12}$ and $Cu_4SnS_4^{13}$ have been reported by several authors.

In this paper, we report the preparation of MnS_2 thin films using simple and cheaper chemical bath deposition technique. There is no report on the deposition of MnS_2 thin films from an aqueous acidic solution at room temperature using the manganese sulfate and sodium thiosulfate acting as a source of Mn^{2+} and S^{2-} , respectively in the presence of

sodium tartrate as complexing agent. We studied the effects of deposition time on the properties of these materials. X-ray diffraction was used to study the structural properties of thin films. Whereas, the morphological and optical properties of the MnS_2 thin films were investigated using atomic force microscopy and UV-visible spectrophotometric measurements, respectively.

Experimental

Preparation of thin films

In this experiment, all the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionised water (Alpha-Q Millipore). Manganese sulfide thin films were deposited onto microscope glass slide using chemical bath deposition method. Prior to deposition, the glass slide was degreased in ethanol for 10 min, followed by ultrasonic cleaning with distilled water for another 15 min and finally dried in desiccators. An aqueous solution of manganese sulfate [$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$] acted as a source of Mn^{2+} , sodium thiosulfate [$\text{Na}_2\text{S}_2\text{O}_3$] supplied S^{2-} ions and sodium tartrate [$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$] was used as complexing agent for depositing thin films. Deposition of thin films was carried out at room temperature in following manner. 25 ml of manganese sulfate (1 M) was mixed with 25 ml of sodium tartrate solution (1M); then, 25 ml of sodium thiosulfate (1 M) was added slowly to the mixture with constant stirring. Finally, the pH was kept at 3 by adding hydrochloric acid. A pH meter was used to control the acidity. The cleaned glass slide was immersed vertically into beaker. The deposition was carried out at different deposition times (2, 3, 6 and 8 days) in order to determine the best deposition time for the deposition of thin films. After the completion of deposition, the glass slide was taken out of the beaker, washed with distilled water and dried in desiccators for further characterization.

Characterization of thin films

The XRD data were obtained from Philips PM 11730 diffractometer using CuK_α ($\lambda=1.5418 \text{ \AA}$) radiation source. The accelerating voltage and current were 40 kV and 30 mA, respectively. Data were collected by step scanning from 25° to 70° with a step size of 0.05° (2θ). The surface morphology was studied by atomic force microscopy. The AFM was carried out with a Q-Scope 250 (Quesant Instrument Corporation) in a contact mode. The optical absorption measurement was carried out in the wavelength range from 350 to 800 nm by using Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was put across the reference path. The absorption data were used for the determination of the band gap energy.

Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the MnS_2 thin films deposited at various deposition times. The manganese sulfide thin films prepared for 2 days show only three peaks at $2\theta=29.2^\circ$, 33.0° and 55.2° corresponding to d -spacing values of 3.06, 2.72 and 1.66 \AA , respectively. These peaks are well match with the Joint Committee Powder Diffraction Standards (JCPDS) data (reference code: 00-065-1844) for MnS_2 compound¹⁴. The lattice parameter values for the dominant cubic structure are $a=b=c=6.097 \text{ \AA}$. The sharp peaks obtained indicate that the materials deposited onto microscope glass slide are polycrystalline in nature. Based on the XRD patterns, the number of MnS_2 peaks is increased to six peaks for the films deposited at longer time (3 and 6 days) which the d -spacing values are well match with the standard JCPDS values. All these peaks corresponding to (200), (210), (221), (311), (023) and (311) reflections are observed as shown in XRD patterns. However, as the deposition time is further increased to 8 days, the MnS_2 peaks reduced to five peaks. The prominent peak occurred at $2\theta=33.0^\circ$ with d -spacing corresponds to 2.72 \AA is detected for all the samples. It indicates that the preferred orientation lies along (210) plane for chemical bath deposited MnS_2 thin films. The peak intensity of the (210) plane increases with increasing deposition time from 2 to 8 days which indicates that the crystallinity of the thin films increases gradually.

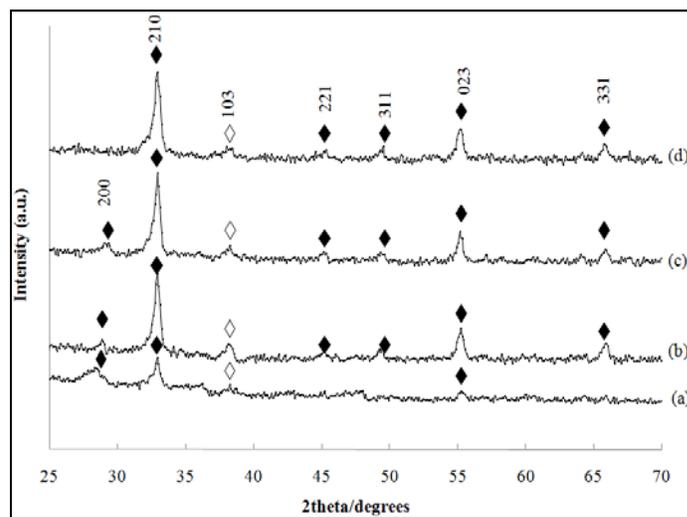


Figure 1: X-ray diffraction patterns of MnS_2 thin films deposited at different deposition times (a) 2 days (b) 3 days (c) 6 days (d) 8 days [◆ MnS_2 ; ◇ SiO_2]

On the other hand, the presence of the silicon dioxide (JCPDS reference No.: 01-074-0201)¹⁵ peaks in the XRD patterns is due to the microscope glass slide used during deposition. Based on the XRD patterns, only single peak occurred at $2\theta=38.0^\circ$ corresponding to (103) plane is observed as shown in Figure 1(a)-(d).

Figure 2 shows three dimensional atomic force microscopy (AFM) images for an area of $20\ \mu\text{m} \times 20\ \mu\text{m}$ for MnS_2 films deposited at various deposition times. The AFM image of the films deposited for 2 days exhibits a smooth surface with spherical shaped grains. The substrate surface is well covered with grains that are uniformly distributed over the surface. The average sizes of smaller grains are found to be in the range between 0.8 and $1.0\ \mu\text{m}$. In contrast, the films deposited at longer time (3, 6 and 8 days) show a mixture of small and large surface features (Figure 2b-d). Several small grains are found to agglomerate and form a few larger grains. The smaller grains have sizes $1.0\ \mu\text{m}$ while larger grains have sizes approximately $3.0\ \mu\text{m}$. We can conclude that the grain size becomes larger with the increasing deposition time.

On the other hand, the root mean square (RMS) roughness was measured using AFM. The surface roughness values for the films deposited for 2, 3, 6 and 8 days are 75, 94, 143 and 156 nm, respectively. The films roughness is unavoidable since the grains were irregular shaped and sized. The thickness of the films was obtained using the AFM technique. Figure 3 shows the variation of film thickness with deposition time. The film thickness increases from 705 to 1220 nm when the deposition time is increased from 2 to 8 days. This indicates that the thickness of the MnS_2 thin films, which were grown onto glass slides at room temperature, is dependent on the deposition time.

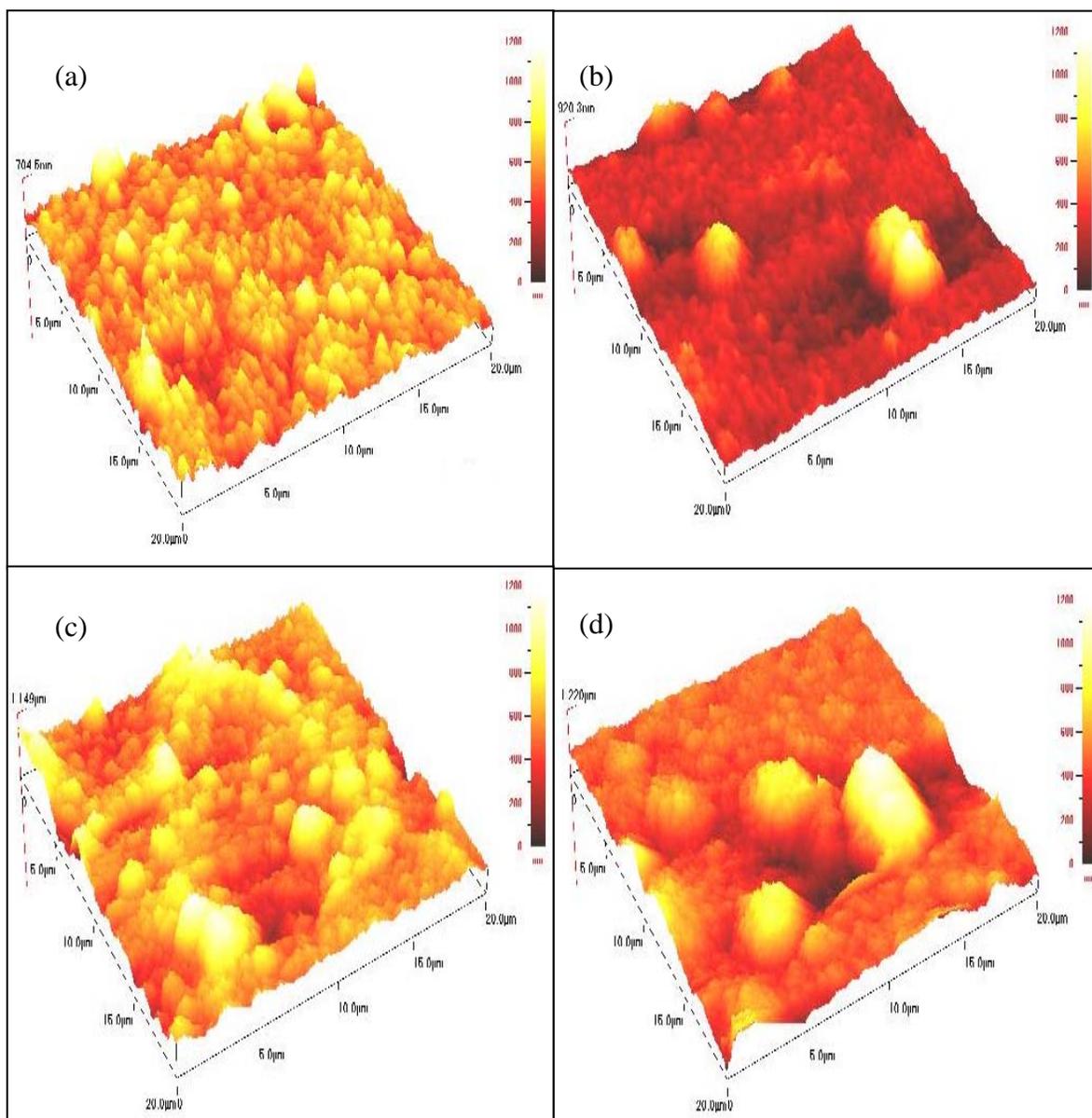


Figure 2: Atomic force microscopy images of MnS_2 thin films deposited at different deposition times (a) 2 days (b) 3 days (c) 6 days (d) 8 days.

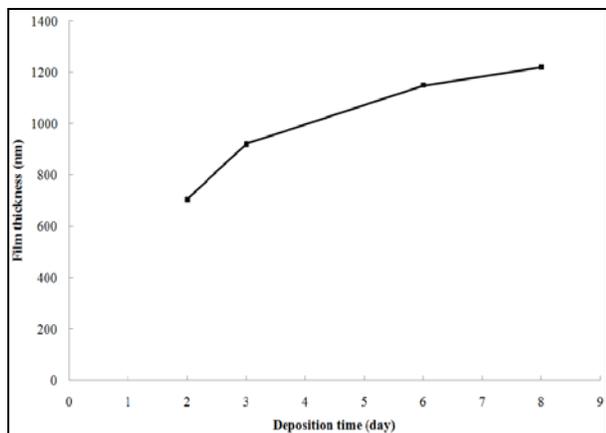


Figure 3: The thickness of MnS₂ thin films with variation deposition time.

The optical absorption spectra of the MnS₂ thin films deposited at various deposition times onto glass slides were studied at room temperature in the wavelength of 350-800 nm (Figure 4). The spectra indicate that the strong absorption is found at shorter wavelength while weak absorption is observed at longer wavelength region. Based on the Figure 4, the films prepared for 8 days show higher absorption characteristics as compared to other deposition times. This may be expected, as the longer the deposition time the more material is deposited onto substrate.

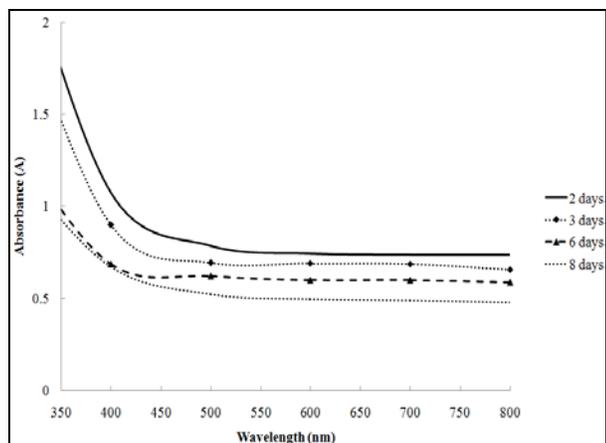


Figure 4: Optical absorbance versus wavelength of the MnS₂ thin films deposited at different deposition times

In order to determine the band gap energy (E_g) of the thin films, the equation of Stern¹⁶ was used.

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu} \quad (1)$$

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4.

The n value is 1 for a direct gap material and 4 for the indirect gap material. The band gap values are obtained by extrapolating the linear portion of the plots of $(Ah\nu)^2$ versus $h\nu$ to $(Ah\nu)^2=0$ as can be seen in Figure 5. The band

gap values obtained are reduced from 3.10 to 2.9 eV as the deposition time is increased (Table 1). These changes have been attributed to the crystallite size or film thickness dependent properties of the energy band gap. This band gap energy is close to the previously reported value⁷ of about 3.88 eV.

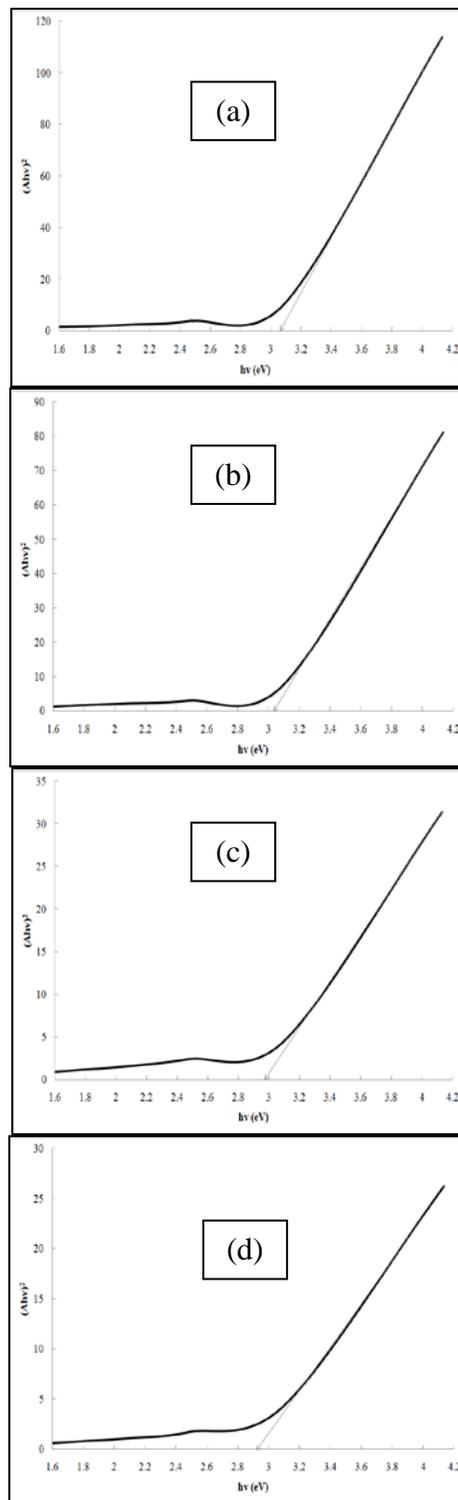


Figure 5: Plots of $(Ah\nu)^{2n}$ versus $h\nu$ for MnS₂ thin films deposited at different deposition times (a) 2 (b) 3 (c) 6 (d) 8 days.

Table 1: Band gap dependence of deposition time of MnS₂ thin films

Deposition time (day)	Band gap (eV)
2	3.1
3	3.05
6	2.95
8	2.9

Conclusions

Manganese sulfide thin films were chemically deposited from manganese sulfate, sodium thiosulfate and sodium tartrate solutions. The number of cubic structure of MnS₂ peaks initially was increased from three to six peaks and then reduced to five peaks as the deposition time was increased from 2 to 8 days based on the XRD patterns. From the AFM results, the grain size, film thickness and surface roughness were increased as the deposition time was increased. From the optical absorption analysis, the band gap energy was decreased from 3.1 to 2.9 eV as the deposition time was increased from 2 to 8 days. The XRD, AFM and optical absorption analysis results suggested that the influence of deposition time on the manganese sulfide thin films was significant.

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References

1. D Fan, X Yang, H Wang, Y Zhang, H Yan. Photoluminescence of MnS thin film prepared by chemical bath deposition. **Physica B**, **337**, 165-169 (2003).
2. D Srekantha Reddy, D Raja Reddy, B Reddy, A Mallikarjuna Reddy, K Gunasekhar, P Sreedhara Reddy. Annealing effect on physical properties of thermally evaporated MnS nanocrystalline films. **J. Optoelectron. Adv. Mat.**, **9**, 2019-2022 (2007).
3. S Agbo and F Ezema. Analysis of chemically deposited MnS thin films. **Pacific J. Sci. Technol.**, **8**, 150-154 (2007).
4. I Oidor-Juarez, P Garcia-Jimenez, G Torres-Delgado, R Castanedo-Perez, O Jimenez-Sandoval, B Chao, S Jimenez-Sandoval. Substrate temperature effects on the growth and properties of γ -MnS thin films grown by rf sputtering. **Mater. Res. Bull.**, **37**, 1749-1754 (2002).
5. Y Zhang, H Wang, B Wang, H Yan, M Yoshimura. Low-temperature hydrothermal synthesis of pure metastable γ -manganese sulfide (MnS) crystallites. **J. Cryst. Growth**, **243**, 214-217 (2002).
6. H Pathan, S Kale, C Lokhande, S Han, O Joo. Preparation and characterization of amorphous manganese sulfide thin films by SILAR method. **Mater. Res. Bull.**, **42**, 1565-1569 (2007).
7. C Gumus, C Ulutas, R Esen, O Ozkendir, Y Ufuktepe. Preparation and characterization of crystalline MnS thin films by chemical bath deposition. **Thin Solid Films**, **492**, 1-5 (2005).
8. A Goudarzi, G Aval, RSahraei, H Ahmadpoor. Ammonia-free chemical bath deposition of nanocrystalline ZnS thin film buffer layer for solar cells. **Thin Solid Films**, **516**, 4953-4957 (2008).
9. M Karimi, M Rabiee, F Moztarzadeh, M Tahriri, M Bodaghi. Controlled synthesis, characterization and optical properties of CdS nanocrystalline thin film via chemical bath deposition (CBD) route. **Curr. Appl Phys.**, **9**, 1263-1268 (2009).
10. K Anuar, W Tan, N Saravanan, S Ho. The effect of bath temperature on the chemical bath deposition of copper sulphide thin films. **Jordan J. Chem.**, **5**, 165-173 (2010).
11. J Chaudhari, N Deshpande, Y Gudage, A Ghosh, V Huse, R Sharma. Studies on growth and characterization of ternary CdS_{1-x}Se_x alloy thin films deposited by chemical bath deposition technique. **Appl. Surf. Sci.**, **254**, 6810-6816 (2008).
12. R Joshi, G Subbaraju, R Sharma, H Sehgal. Pb_{1-x}Fe_xS nanoparticle films grown from acidic chemical bath. **Appl. Surf. Sci.**, **239**, 1-4 (2004).
13. K Anuar, N Saravanan, K Zulkefly, S Atan, W Tan, S Ho. Influence of complexing agent (Na₂EDTA) on chemical bath deposited Cu₄SnS₄ thin films. **Bull. Chem. Soc. Ethiop.**, **24**, 259-266 (2010).
14. J Hastings, N Elliott, L Corliss. Antiferromagnetic structures of MnS₂, MnSe₂ and MnTe₂. **Phys. Rev.**, **115**, 13-17 (1959).
15. A Weiss and A Weiss. Uber Siliciumchalkogenide. VI. Zur Kenntnis der faserigen Siliciumdioxid- Modifikation. **Z. Anorg. Allg. Chem.**, **276**, 95-112 (1954).
16. F Stern. Elementary theory of the optical properties of solids. **Solid State Phys.**, **15**, 299-408 (1963).