

Study the Influence of Chemical Treatment on the Compositional Changes and Defect Structures of ZnS Thin Film

N. Dahbi, D-E. Arafah

Abstract—The effect of chemical treatment in CdCl_2 on the compositional changes and defect structures of potentially useful ZnS solar cell thin films prepared by vacuum deposition method was studied using the complementary Rutherford backscattering (RBS) and Thermoluminescence (TL) techniques. A series of electron and hole traps are found in the various as deposited samples studied. After treatment, perturbation on the intensity is noted; mobile defect states and charge conversion and/or transfer between defect states are found.

Keywords—chemical treatment, defect, glow curve, RBS, thin film, thermoluminescence, ZnS, vacuum deposition

I. INTRODUCTION

ZINC sulfide (ZnS), is well known as one of the promising II–VI compound semiconductors of a broad-band luminescence from the near UV to the near IR, therefore it is of prime interest for light emitting optoelectronic devices [1]. Over the past decade, the study of extremely thin films and interfaces has become increasingly important from the perspective of both fundamental physics and technology. However, there are few quantitative analytic techniques with sufficient sensitivity and resolution to measure unambiguously some basic properties such as the elemental composition of thin films (less than 10 nm) and interfaces, especially if these films or interfaces are buried within the solid. The Rutherford backscattering technique (RBS) is one of these tools that uses elastic scattering of 0.1-3 MeV charged particles to analyze the surface and the near surface regions within a few micrometers of solids [2]. The incident ions suffer energy losses while moving in the target; thus losing energy until eventually stopped within the target. The backscattered particles convey quantitative information about individual elements present and depth profile distribution, typically the RBS method is not only used to determine thin film thickness and composition as a function of depth, but also to determine lattice disorder and location of lattice impurities when combined with channeling.

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This is particularly useful in the analysis of crystalline thin film materials [3],[4]; the most extensive use of the RBS technique finds itself in various fields of electronic and optical materials and applications, e.g. special coatings and in the study of various physiochemical processes on solid surfaces [2]. Further pursuance on the properties can be made by complementary techniques, for example: investigation by Thermoluminescence (TL) can provide some useful information about the surface and interface states that may explain the size dependence of the surface defects. The method is, however, a very sensitive technique for the detection of traps or defects and information about charge carriers involved in emission and recombination processes is possible [5], [6]. The main objectives of this research are to prepare a ZnS thin films deposited on quartz that are potentially useful in solar cell application; by vacuum deposition method then investigate the composition of the films, defects and the influence of chemical treatment in CdCl_2 by RBS and TL techniques.

II. EXPERIMENTAL DETAILS

In the preparation of our thin films; a 0.07- μm -thick ZnS film was first deposited on Quartz substrate by vacuum deposition with a typical working pressures of 10^{-4} Pa were used during evaporation, this was then dipped in 1% CdCl_2 methanol solution for about 30 s to improve the conductivity, then dried with an infrared lamp, and then rinsed in the deionized water. Rutherford backscattering (RBS) was used to characterize the films, using 2 MeV α -particles beam supplied from the University of Jordan Van de Graaff accelerator (JOVAC). Detection of backscattered particles was done using normal incidence and a scattering geometry with angle 135 relative to the incident beam and the reflected particles were collected using a silicon surface barrier detector of 12keV resolutions and active area of 50. To assist in the evaluation, Rump simulation was used such that estimates of the layer thickness and compositions even with extremely complex samples are possible, [7]. Reliable data are obtained from RUMP since the parameters are derived from the experiment.

The system employed for TL-detection was a commercial Pitman TOLEDOO TLD 654 READER, with a research module to control the heating cycle. The glow curves (GL-curves) were obtained from the simultaneously recorded

signals of TL-response and temperature; both are functions of time. The Readout system represents all necessary information to obtain the intensity of emitted light versus temperature glow-curve (GL-curve) out on platinum planchet at linear heating rate of 2°C s^{-1} . All the produced samples were irradiated using α -source (2 MeV); deconvolution of the GL-curves was used to separate the overlapping dosimetric peaks.

III. RESULT AND DISCUSSION

The Rutherford backscattering (RBS) technique is now a firmly well established as one of the most powerful methods to investigate the bulk composition and stoichiometry of materials and consequently any structural changes in their composition as a result of ion beam modifications.

A typical RBS spectrum, of ZnS film deposited on quartz is shown in Figure 1 before and after chemical treatments; the simulation obtained by RUMP calculations is also shown as a solid curve.

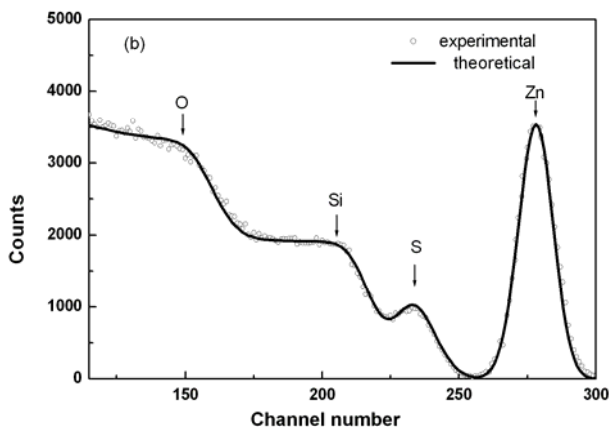
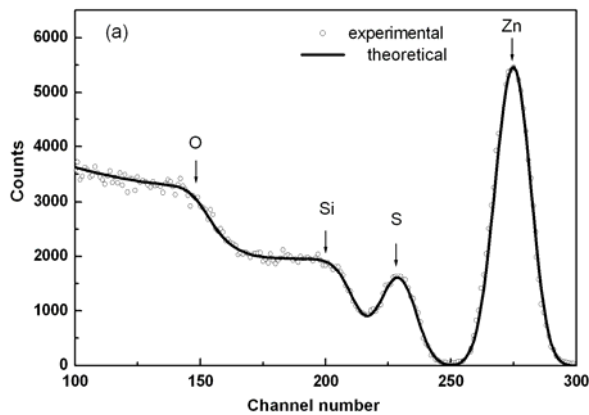


Fig. 1 Typical 2 MeV RBS spectrum of ZnS thin film deposited onto quartz glass: (a) before chemical treatment; (b) after chemical treatment

Clearly, the calculated curve well and consistently reproduces the experimental data (open circles); it is however noted that the measured ZnS layer is almost 30 % larger than the nominal deposited thickness (70nm) as measured by a quartz crystal monitor; in addition the measured stoichiometric ratio of Zn to S is preserved at unity. Furthermore, the excellent match between simulation and experiment was only attained with the incorporation of a slight amount of Oxygen and Silicon within the ZnS layer. The percentages of both O and Si involved are estimated by 10% and 20 % respectively; such amounts indicate that the matrix is an active ingredient that may mix within the film components at room temperature, even prior to any chemical or heat treatment, this is justified by recognizing and observing that the interface boundary near the front edge of the substrate is trailing towards higher energies. The trailing edges of either film component are also exhibiting tailing towards lower energies or larger depth values; one possible mechanism by which this can take place is via a concentration gradient process.

Figure 1(b) represents the typical RBS spectrum of ZnS film after treatment in 1% CdCl_2 methanol solution for 30s, the post chemical treatment indicates that minor changes are taking place, this is noted on the signals belonging to the substrate but revealing that the material bulk has affected sample insignificantly. On the other hand, marked changes are realized to affect the film components: reduction of signal heights is noted; in particular, the reduction noted was about 35 % on the Zn signal and an almost 40% reduction corresponding to the S signal. This clearly indicates that, to within experimental uncertainties, an almost the same ratio loss, namely (1:0.8). Such a ratio is preserved after treatment, indicating an insignificant stoichiometric influence on the film components. In any case, incorporation of layer that is 90nm thick from the substrate is noted. The loss of signal from the film component is possible by the reactive solution which is known to act as a crystallizing agent, the latter also results in larger grain size particles that may increase and enhance the efficiency of solar cells [8],[9]. Alternatively, probing a crystalline matrix or that which may exhibit crystalline behavior can result in a drop in the scattered yield. However, close examination of the substrate indicates that a random behavior texture is maintained, one possible explanation is to assume that only the film is exhibiting a crystalline behavior, such that the analyzing beam is probing a lower density material or better oriented film. The larger grain size films induce stresses within the structure and high density concentrations of structural defects are expected and formed.

Typical glow curves obtained from ZnS samples are shown in Figure 2; Deconvolution results in separating four major peaks labeled P_1 through P_4 are also shown, such isolated peaks give rise to the emission and are correlated to crystal defects within the material.

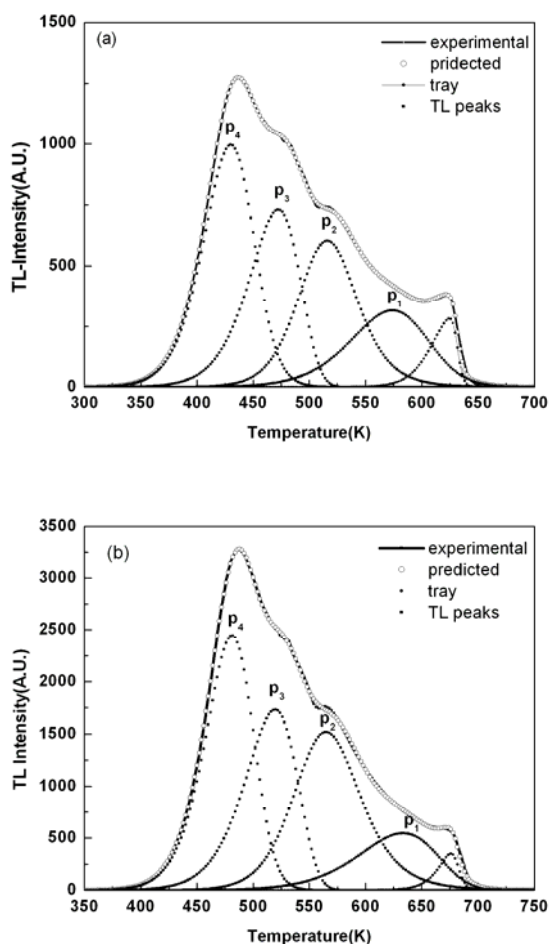


Fig. 2 Glow curve of ZnS thin films: (a) before chemical treatment, (b) after chemical treatment. Separated peaks represent deconvolution procedure using least square method.

Comparison between the glow curves before and after treatment indicates that after chemical treatment perturbation on the intensity is noted such that in some cases it is doubled or more. The number of peaks, however, is preserved but there exist changes in their detected positions and perhaps their type. Literature indicates the formation of clusters and complex defect structure proceeding chemical treatment; the increase of intensity is solely due to incorporation of chlorine; oxygen may also have a role in enhancing the TL emission process by vacancy type defects [10]. However, no further statement is given here without identifying its role; but, it is present and we have a clear evidence of its presence by refereeing to the RBS data. One explanation may be presented by moving the passivity of the surface towards an oxide layer that acts to reduce surface states from the sample; the incorporation of chlorine and oxygen which act as shallow acceptors and the structural changes observed results in the creation of additional defect complexes [11]. Variations in the centers of peak positions P_2 , P_3 , and P_4 express shifts towards higher temperatures by an almost 50K except for peak P_1 ,

which exhibits a larger shift of some 67K. The initial concentration of trapped electrons within the defects centers was however noted to vary. The percent has increased by about 96%, 194%, 145% and 85% for P_1 , P_2 , P_3 , and P_4 respectively. Such variations in the population of electrons within the traps are an indication of mobile defect states and charge conversion and/or transfer between defect states such that very shallow states and deep level states are emptying to moderate defect states. This has two main advantages on the efficiency, first: defect states are becoming more stable since the temperature at maximum is increased and second, unwanted deep level states as well as surface defect states are minimized or even eliminated. Consequently, a better efficiency becomes always an eventuality. It is worth mentioning that these observations are consistent with the RBS results, which also indicate a structural changes taking place following chemical processing. Yazici [12] found that the intensity of TL-signal from ZnS thin films strongly depends on thin film production conditions; particularly, when the concentration of Cl impurities increases.

IV. CONCLUSION

The composition of ZnS thin film deposited onto Quartz substrates has been studied by RBS technique, irradiative defect states resulting from this thin films have also been investigated using TL method, A series of traps have been identified, charge transfer and conversion between traps is noted, it was observed also that the position of trap states and intensity of TL GCs of these films changes after chemical treatment in $CdCl_2$. It was concluded that, in spite of significant effects of chemical treatments on the structure of defects and thereupon on the intensity of TL GCs.

REFERENCES

- [1] L.V.Zavyalova, A.I. Beletski, and G.S.Svechnikov, *Semicond.Sci Technol.* vol. 14, pp. 446-449, 1999.
- [2] R. Tesmer, M. Nastasi (Eds.), *Handbook of Modern Ion Beam Materials Analysis*, MRS, Pittsburgh, 1995.
- [3] W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry*, Florida: Academic Press, 1978.
- [4] J. S.Williams, and J. M. Poate, *Ion Implantation and Beam Processing*, Australia: Academic Press, 1984.
- [5] S. W. S McKeever, and R. Chen, *Rad. Meas*, vol. 27, no.(5/6), pp.625-661, 1997.
- [6] P. D .Townsend and A. P. Rowlands, *Radiation Protection Dosimetry*, vol. 84, no. 1-4, pp. 7-12, 1999.
- [7] L. R .Doolittle, *Nucl. Instru.and Meth, B 9*, vol. B9, no. 3, pp.344-351, 1985.
- [8] V.Komin, B.Tetali, V.Viswanathan, S. Yu, D. L. Morel, and C. S. Ferekides, *Thin Solid Films*, vol. 431-432, pp.143-147, 2003.
- [9] D.E. Arafah, and R. A. Bitar,, *Solar Energy Material and Solar cells*, vol. 64,pp. 45-54, 2000.
- [10] N. Yazici, *Tr. J. of Physics*, vol. 22, pp. 415-419, 1998.
- [11] J.Krustok, J.Madasson, K.Hiilt, and H.Collan, *Journal of Material Science*, vol.32, no.6, pp.1545-1550, 1997.
- [12] N. Yazici, M. Oztas, and M. Bedir, *Journal of Luminescence*, vol.104, pp.115-122, 2003.