Free Standing Chalcogenide /Polymer Nano Composites

for Photonic Applications.

Tintu.R¹, Aparna V², Hema Vijayan S³, Sreena CV⁴

¹T K Madhava Memorial college, Nangiarkulangara Alappuzha, Kerala, (India)

Abstract

In this paper we are presenting the optical characterization Er doped chalcogenide nanocomposte and thermally evaporated chalcogenide film. Chalcogenide glass-polymer hybrid materials may be created through the incorporation of compatible polymers in the chalcogenide solution phase. It is shown that it is possible to tune the optical and mechanical properties of these coatings by tailoring the glass chemistry/polymer content over a broad range, important for applications in IR optical coatings and as interfacial materials where thermal and mechanical property matching is critical. The presence of rare earth makes it a potential materials for fiber optic amplifiers operating at 1.3 μ m and 1.5 μ m telecom windows. In this context, we present a work in search of new materials based on amorphous rare earth doped nano composite.

I. INTRODUCTION

Possibilities of chalcogenide and polymer films as an alternative to dielectric materials have been developed in recent times. The omnidirectional Quarter Wave Stack (QWS) devices can be fabricated as multilayers using thermal evaporation of high index chalcogenide glasses and the polymers which form a low index films. A permutation of highly transparent chalcogenide and polymer films enables these QWS elements to cover the wavelength ranges reaching from the visible to the infrared spectral regions including telecommunication wavelengths. In order to fabricate the above mentioned mirrors and filters certain conditions have to be contented. An initial step for the fabrication of devices by stacking is the awareness of the optical parameters of the layers and it is discussed in this section. By knowing the optical properties of the single layer and double layered films one can easily design the thickness and number of layers required for required application. In recent years, Optoelectronics is widely considered to be the field in which lies the future of communication. Silicon which was mostly responsible for the growth of electronics was found to be not feasible for optoelectronic applications due to indirect band gap. Gradually the focus shifted from crystals to non crystalline solids. The amorphous chalcogenide glass has promising optical properties, but here exist certain challenges associated with the use of chalcogenide glass like toxicity, durability and large coefficient of thermal expansion. This can be overcome by making composite films using chalcogenide glass. Low dimensional inorganic/polymeric nano-composites represent an important and growing class of hybrid materials with promising physical and optical characteristics [1-3]. At the same time it was shown that the photoinduced changes in chalcogenide glasses and polymers may be due by the atom displacements in these materials. Because the organic polymers exhibit high photoinduced changes and low stability and on the

contrast, the chalcogenide glasses - low photoinduced effects and good stability, the combination of these properties by creation of new composites based on chalcogenide glasses and polymers can allow to obtain new materials with new multifunctional properties[4,5]. Doping of chalcogenide glasses with tin and rare-earth ions increase the stability of amorphous As2Se3 thin films against light irradiation and heat treatment[6]. The chalcogenide glasses As2S3 and As2Se3 doped with rare earth ions are perspective materials for fiber optics amplifiers, recording media for high-resolution diffraction gratings, planar-integrated optical elements, alloptical switches, etc. A variety of nanocomposite materials based on As2S3 and GeSe3 chalcogenide glasses was formatted under specific UV irradiation conditions. It was established that applying lasers as a tool for photothermal synthesis it is possible to create a variety of multicomponent composites with new functional characteristics. Moreover, using the chalcogenide glass and commercial polymers, different integrated waveguides with low-loss (~0.2 dB/cm) were realized. Recently new nanocomposites based on semiconductors (PbS) and polymer, chalcogenide glasses (As2S3) and polymer for electroluminescence and different diffractive elements were investigated. High photoluminescence gain from Nd3+-ion-implanted As2S3 planar waveguide at 1090 nm was observed. By thermal evaporation and subsequent ion implantation were obtained thin films of Arsenic Seleniumglass doped with Er3+, which shows a luminescence peak situated at 1536 nm. In such way it was demonstrated that the combination of thermal evaporation and ion implantation is an efficient method for the fabrication of rare-earth doped waveguides, avoiding any solubility limitation. In order to increase the absorption length the method is apply to obtain multilayer structures. For this reason, investigation of new nanocomposites thin film structures based on chalcogenide glasses doped with rare earth ions and mixed with polymers is actually[6].

In the present work, nanocolloid of chalcogenide glass was prepared using GeSeSb chalcogenide glass and nbutyl amine. The prepared nanocolloid solution and polyvinyl acid were mixed in different proportions using a magnetic stirrer. Using these mixtures films were formed. The formation nano particles were monitored by visualizing colour change and it is confirmed by UV Visible spectrometer. Every film has a characteristic Transmittance (T) and Reflectance (R). This spectral dependence of transmission and amount of transmission and reflectance was found out using a spectrometer. This help to find absorption co-efficient of thin film and dependence on wavelength. Using transmittance and reflectance of the film absorption co-efficient is calculated and also band gap can be calculated.

II. EXPERIMENTAL

In order to prepare the solution of Chalcogenide glass with the solvent n-Butylamine, first step involves the meticulous cleaning of the equipments such as beaker, standard flask, etc. The equipments were introduced into a soap solution for removal of visible diet and body oils which may have been deposited during the handling. Acetone was used to etch glass and clean it thoroughly. After a brief treatment with acetone the equipments were kept in laboratory oven to remove moisture. Bulk chalcogenide glass(GeSbSe0.2%Er) prepared by melt quenching method is 1st weighed on the weighing machine. 0.106 gm of bulk chalcogenide sample is taken and grinded manually to make power form of nano size to increase the surface area and therefore to shorten the dissolution time. Now in order to make solution I, we took 0.106 gm of powdered chalcogenide in 20 ml of n-Butylamine. The dissolution is carried out inside a sealed glass container of 250 ml capacity to prevent solvent

evaporation. A magnetic stirrer is used to expedite the dissolution process (to dissolve the solution completely and homogeneously). We have given continuous magnetic stirring of approximately an hour to the sample. After the solution got completely dissolve we got a gray red colour solution.Similarly, prepare a solution of chalcogenide glass with 40 ml n-butyl amine (solution II).Then take 40ml n-butyl amine and add 5 ml of the above prepared solution(solution II), let us call it as solution III.Take 100 ml of battery water in a beaker and add 15 g of PVA with constant stirring using a magnetic stirrer at 70 degree Celsius in the presence of UV light for about 1 hour.Then take 15 ml of the above prepared viscous solution of PVA and battery water in a beaker and added 5 ml of solution I with constant stirring using a magnetic stirrer and is allowed to form film 1.By following the same procedures described above, prepare film 2 of solution II and film 3 of solution III.

III. RESULTS AND DISCUSSIONS

The transmission spectrum of the samples fabricated obtained from a spectrometer is as shown in Figure 1. Optical transmission (T) and reflection (R) are very complex functions and strongly depend on the absorption coefficient. Various optical parameters are calculated for the prepared thin film using a straight forward method proposed by Swanepoel[8-10]. The optical energy gap has been determined from plot 2 (for c2) by the intercepts of extrapolations to zero with the photon energy axis $(\alpha hv)^{1/2} \rightarrow 0$ (i.e. Tauc extrapolation). The optical energy gap has been tabulated in table 1. The variation of k with wavelength for the film is shown in Figure 3. The decrease in refractive index with wavelength shows the normal dispersion behavior of the material as in figure 4. The real (ε_r) and imaginary (ε_i) parts of the dielectric constants for a thin film are calculated with the help of refractive index and extinction coefficient. Real part of dielectric constant is calculated using the relation $\varepsilon_r = n^2 - k^2$. while the imaginary part is calculated using, $\varepsilon_i = 2nk$. The complex dielectric constants are fundamental intrinsic material property. The real part is associated with the term that how much it will slow down the speed of light in the material and imaginary part shows how much a dielectric absorb energy from electric field due to dipole motion.



Figure 1 Transmission spectra of fabricated films



Figure 2 Plot of absorption coefficient for films,c1,c2,c3









Figure 4:Plot of refractive index, optical conductivity, real part of dielectric constant(ϵ_r), imaginary part of dielectric constant(ϵ_i), of c1 film.

Table 1: The bandgap(E_g), width of localized states (E_e), refractive index (n at 1000nm), extinction coefficient (k at 1000nm), optical conductivity (σ at 1000nm), real part of dielectric constant(ϵ_r), imaginary part of dielectric constant(ϵ_i), of films.

	Thermal	C1	C2	C3
	evaporated			
$E_g(eV)$	1.80	2.5	2.76	3.02
E _e (meV)	0.66	645	430	267
n	1.71	1.87	1.75	1.72
k	0.129	$0.07*10^{-4}$	1.02*10-4	4.99*10 ⁻⁵
σ (s ⁻¹)	$1.58*10^{11}$	$5.98*10^{10}$	5.26*10 ¹⁰	$2.58*10^{10}$
$\epsilon_r (eV)$	10.38	3.130	2.978	2.652
$\epsilon_i (eV)^* 10^{-4}$	0.23	4.01	3.511	1.725

The variation of both ε_r and ε_i with λ follows the same trend as that of refractive index and extinction coefficient. The optical conductivity is determined using the relation $\sigma = \alpha n c/4\pi$ where 'c' is the velocity of

light. Optical response is most conveniently studied in terms of optical conductivity and it has the dimensions of frequency, which are valid only in Gaussian system of units. The optical conductivity directly depends on the absorption coefficient and refractive index and is found to increase sharply for higher energy values due to large absorption coefficient as well as refractive index. The refractive index has been found to decrease with the decrease in concentration of the chalcogenide glass content. It was shown from the studies that the addition of inorganic semiconductor into the polymer results in fabrication of new composite films with low cost. The investigated new composites are prospective for different photonic devices and for nonlinear optical applications.

III. CONCLUSION

We have fabricated free standing films which depends wide applications in film technology using new low-cost, scalable method method . The optical constants of fabricated films were calculated from the transmission spectra and reflection spectra using Swanepoel method. The optical parameters, refractive index (n) and extinction coefficient (k) have been calculated in the wavelength range 700–2000 nm by analysing the transmission spectrum. The studies show that the polymer GeSeSb +Er composite films are promising candidates for optical limiters and for the development of nonlinear optical devices. The optical energy gap has been estimated using the Tauc method. The energy gap of the films was found to depend on grain size which is inversely proportional to concentration of the colloidal solution used. Thus depending on the concentration of the nano colloid solution used for the fabrication of nano composite films, varying nonlinear response can be obtained, enabling a pathway to new materials for optoelectronic devices.

IV. ACKNOWLEDGEMENT

We acknowledge Kerala State Council for Science, Technology & Environment for the financial support through 62th student project.

REFERENCES

- Victor K. Tikhomirov," Photoinduced e€ ects in undoped and rare-earth doped chalcogenide glasses: review", Journal of Non-Crystalline Solids., 256&257, 328-336(1999).
- [2.] Angela B Seddon, Zhuoqi Tang, David Furniss, Slawomir Sujecki, and Trevor M Benson," Progress in Progress in rare-earth-dopedmid-infrared fiber lasers" "Optics Express, 18, 26704-26719 (2010).
- [3.] Yu.S. Tver'yanovich and A. Tverjanovich," Rare-earth doped chalcogenide glass", Semiconductors and Semimetals., 80, 169-207(2004).
- [4.] A. B Seddon," Chalcogenide glasses: a review of their preparation, properties, and applications,"J. Non-Cryst. Solids, 184 44-50 (1995).
- [5.] Sanghera J.S et al., "Development and infrared applications of chalcogenide glass optical fibers," Fiber Integrated Opt., 19 [3], 251 - 274 (2000).
- [6.] Schweizer T. et al.," Properties of dysprosium doped GaLaS fiber amplifiers operating at 1.3 μ m," Optics Express, 1, 102–107 (1997).

- [7.] R. Tintu, K Sulakshna, K Saurav, V P N Nampoori, P Radhakrishnan and Sheenu Thomas,
 "Ge28Se60Sb12 /PVA Composite Films For Photonic Applications", Journal of Non-Oxide Glasses., 2, 167-174 (2010).
- [8.] R. Tintu, V.P.N. Nampoori, P. Radhakrishnan, Sheenu Thomas, "Non linear Optical Characterization of erbium doped Ge- Sb- Se thin films, Discourse Science (In press).
- [9.] R. Tintu, V.P.N. Nampoori, P. Radhakrishnan, Sheenu Thomas "Nanocomposite thin films of Ga5Sb10Ge25Se60 chalcogenide glass for optical limiting applications", Optical Materials., 33, 1221– 1225 (2011).
- [10.] K. S. Bindra, H. T. Bookey, A. K. Kar, B. S. Wherrett X. Liu and A. Jha," Nonlinear optical properties of chalcogenide glasses: Observation of multiphoton absorption", Applied Physics Letters., 79, 1939-1941 (2001).