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Novel Photo-Response Properties Of Synthesized Nanocrystalline Bas: Ce^{+3}-Ions Thin Films

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Abstract:
SILAR *(Successive Ionic Layer Adsorption and Reaction) technique was used to synthesize Ce^{+3}- ions (2at. %, 4at.%, 6at.%, 8at.% and 10at.%) doped BaS thin films (0.4M) on ultrafine Silicon wafer substrates using AR grade chemicals, Barium acitate, $Ba(CH_3COO)_2$ $2H_2O$ (AR Grade),Thiourea, $CS(NH_2)$ and Cerium nitrate, $Ce(NH_3)_3$ as doping agent in presence of Polyvinyl Alcohol (PVA) and Ammonia solutioin (AS). The as grown films were annealed at 200^0C in microwave oven for 24hrs for crystal growth. Gap type silver electrodes were vacuum deposited across the BaS doped Ce^{+3} - ions (CIs) thin films fabricated in the form of Ag/BaS/Ag configuration. The photoelectrical properties in the films were studied under constant illumination of white light (WL) of different intensity and d.c. applied bias (AB) in vacuum pressure ≈ 2.67Pa. The I-V characteristics of the grown films doped 2 at. %, 6 at.% and 10 at.% of CIs at (-) 180V-0-(+) 180V showed distinct linearity and symmetrical about zero applied bias and confirmed junction ohmic nature interface between the BaS films- metal electrode contacts. Photoresponse properties – photocurrent and photosensitivity of the BaS thin films doped at different CIs concentrations under different intensity of WL, AB and ambient temperatures (AP) in vacuum were observed linear dependent on the doped CIs - concentrations, intensity of WL, AB and grain sizes. The photo-response characteristics in the films were found due to predominating by bimolecular recombination of carriers.*

Keywords: *BaS thin films, FESEM, XRD, Photocurrent, photosensitivity*

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I. Introduction:

Bulk barium sulphide (BaS) is an inorganic compound semiconductor having wide indirect energy gap of E_g = 4.0eV that belongs to II-VI metal chalcogenite group. Intensive research works on synthesized BaS doped with rare earth activators are found rare cases in national and international levels. BaS can be synthesized by different deposition techniques- (i) chemical bath deposition, (ii) electrodeposition, (iii) hydrothermal deposition (iii) photoelectrochemical (iv) spray pyrolysis (v)Sputtering (vi) thermal evaporation (vi) successive ionic layer adsorption and reaction (SILAR).(vii) Sol-gel method. Among these, SILAR technique proves most cost effective and less man power and time consumption [1,2,3]. Basically, II-VI compounds have greater potential applications in the fields of light emitting diodes (LEDs), laser diodes (LDs) and other photoelectronic devices [4,5,6]. BaS is most active, moderately water and acid soluble compound.

Photoconductivity in a material is the manifestation of photo-electrical conductivity caused by interaction of light quanta with the material and absorption of quantum of energy which results in the production of free mobile carriers. Under a suitable applied electric field, a constant photocurrent is generated in the external circuit. This photo-electrical process finds several applications in electronic industry and research [7]. In this proposed work, BaS compounds will be chemically synthesized and doped with rare earth Ce^{+3} ions at different doping concentrations by SILAR method at the nano-scale and the novel photo-response and photoconductivity properties will be investigated for electronic device and applications.

II. Materials And Method

Material Synthesis

In synthesis process (SILAR), high purity (i) Barium acitate, $Ba(CH_3COO)_2$ $2H_2O$ (AR Grade),was used as Ba^{+2} – cation source (ii) Thiourea, $CS(NH_2)_2$ (AR Grade) as S^{-2} - anion source (iii) Cerium nitrate, $Ce(NH_3)_3$ as doping agent, (iv) Ammonia solution to adjust the pH of the precursor solution (v) Polyvinyl alcohol (PVA) as matrix for controlling the growth and stabilization of BaS thin films on the substrates.

Preparation of 0.2M $Ba(CH_3COO)_2$ solution:

We prepared 0.2M $Ba(CH_3COO)_2$ by dissolving 5.11gms of it in 500ml DI water and stirred thoroughly for 30mins for reserved solution.

Preparation of 2wt.% PVA solution:

We dissolved 2gms. of PVA in 100ml DI water and the resultant solution was stirred for 1hr. till PVA dissolved. The precursor was divided into two beakers.

Preparation of 2 at. % Ce^{+3}-ion solution:

By calculation, 0.34gm of Ce $(NO_3)_3$ was dissolved in 50ml DI water to obtain *2at. % Ce^{+3}*-ionic solution. Now, 50ml of Ba $(CH_3COO)_2$ solution was mixed with 50ml PVA solution and 50ml of *2at. % Ce^{+3}*-ionic solution and the resultant solution was refluxed for 5mins. The properly cleaned silicon wafer substrates (5nos.) were fully immersed vertically in the precursor solution for 24hrs when Ba^{+2}-cations were adsorbed onto the substrates. The substrates were removed gently, stabilized for 10mins and then rinsed in running DI water for removal of unwanted course Ba^{+2} –ions.

Preparation of 0.2M $CS(NH_2)_2$ solution:

We prepared 0.2M $CS(NH_2)_2$ solution by dissolving 1.5gms of it in 500ml DI water with constant stirring for 30mins. Then, a few drops of ammonia solution were added to yield alkalinity at pH-10. The precursor was heated to 70^0C for 1hr. with constant stirring till $CS(NH_2)_2$ dissolved completely and finally cooled down to room temperature. The substrates were vertically immersed again into the precursor solution for 24hrs when S^{-2}-anions were adsorbed onto the Ba^{+2}-ions pre-deposited substrates. The two opposite Ba^{+2} and S^{-2}-ions reacted to form BaS (0.2M) equimolar thin films doped Ce^{+3} at *2 at.%*. The substrates were gently removed and finally rinsed in running DI water, stabilized at room temperature and then annealed at 50^0C for 24hrs. Similar procedures were carried out for synthesis of *4,6,8* and *10at.% Ce^{+3}* ions doped BaS thin films.

Measurements of photoresponse currents and sensitivity

The primary requirement is to ensure good ohmic contacts between the film and electrodes for photoconductivity measurements. For achieving this, a photo grade purity Ag electrodes of 5.0 x 10.0mm2 sizes were uniformly vacuum deposited over doped BaS thin films using a properly designed mica-masks inside **HINDHIVAC 12 A** 4 vacuum Coating Unit under vacuum pressure 1.33 x 10^{-4}Pa to achieve Ag/ BaS /Ag gap type cell configuration with 5mm inter-electrode spacing. The cell configurations were successively mounted on a suitably designed mica

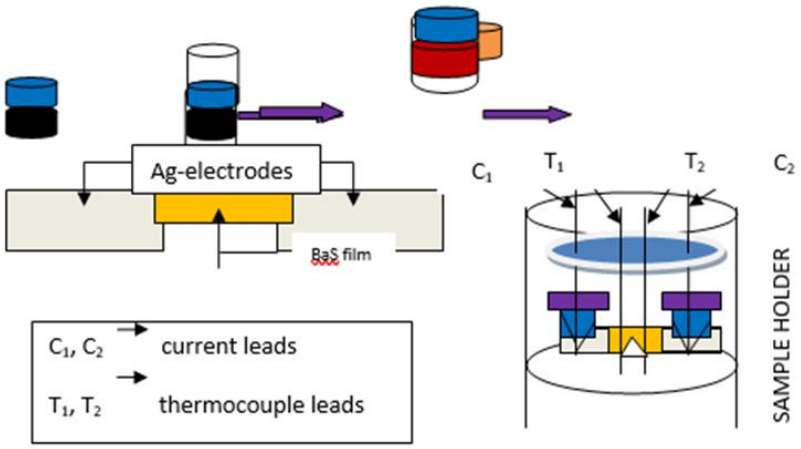

Fig.1. Fabrication steps and electrical connections inside sample holder.

sample mount and then suspended inside a continuously evacuated air sealed glass sample holder using thin enameled copper wires under vacuum pressure ~ ≈ 2.67 Pa achieved by means of a double stage rotary pump. An optical dark background focusing arrangement was made for uniform illumination of the sample with a white light (WL) intensity. A tungsten halogen lamp (**250W-24V**) attached with a parabolic focusing mirror was used for the light source. An APLAB-Luxmeter (**model 5011S**) was used for measuring the intensity (φ) of the incident WL.

A constant WL intensity of 22 x 10^3 Lx was incident on the sample inside the vacuum ambient temperature. The dark currents (I_D) and the currents under illumination (I_L) were measured with the help of high

input impedance (~$10^{14}\Omega$) **ECIL Electrometer Amplifier** under different d.c. bias voltages obtained from a number of series connected dry cells of emf 9 volts each.

III. Results And Discussion:

Material characterization

For study of photocurrent, spectral -response and photoconductivity properties in the BaS films, primary work is to confirm the ohmic contacts between the as deposited BaS thin films and the vacuum deposited electrodes, which will be observed from the photocurrent (I_{ph}) vs. applied bias (V)in steps of 9Volts plots. The I-V characteristics of the BaS : Ce^{+3}-ions at selected doses 2at.%, 6at.% and 10 at.% is shown in the representative Fig.2.

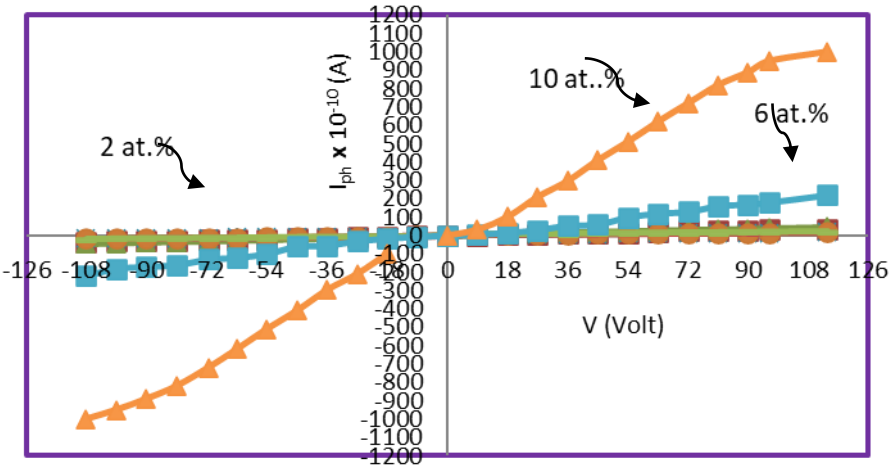

Fig.2. I-V characteristics of BaS:Ce^{+3} -ions thin films at 2at.% , 6at.% and 10 at.%.

Photocurrent (I_{ph}) is defined as the effective current due to the flow of carriers in the material under illumination and dark given by $I_{ph} = I_L - I_D$, where I_L is the current under illumination and I_D is the dark current produced by the minority carriers when the light is switched off. The distinct observed linearity and symmetrical nature of I_{ph} about the zero applied voltage in the I-V characteristics showed that the electrode – film contacts are ohmic and electrode-film junction barriers are rectified in the whole range of applied bias.

Characterization of dopents and bias on I_{ph}

The strength of I_{ph} measured in the material lies of the order of 10^{-8} to 10^{-10} A . Therefore, it is convenient to take log of Iph and log of φ to characterise under different CIs concentrations and AB. The variations of log I_{ph} vs. Logφ for two representative BaS samples doped 2 at.% and 8 at.% of Ce^{+3} ions under applied bias 36V, 63V and 90V have been shown in Fig.3. The current and the excitation light intensity of WL is related by the power law relation [8,9]

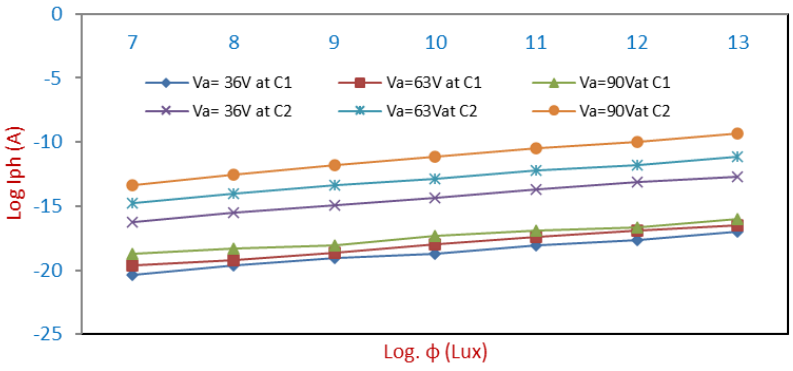

Fig.3. Photocurrent vs. light intensity in BaS thin films :C_1-2at.%, C_2=8at.% at different bias.

$I_{ph} \propto \varphi^k$ (1)

where the exponent k represents a number which depends on the basic nature of the material under investigation. The value of k can be calculated from the slope of Log *Iph vs. Log Φ* plots in the given ambient condition of the host material. Here φ is defined as the number of photons incident per second on unit surface area of the material under investigation. The variation of Log *Iph vs. Log φ* in the material. The values of exponent k calculated from such plots are given in Table - 1. The results show that the values of k in the host samples are not different from the mean value 0.59. The exponent relation (1), therefore, can be expressed in the

Table-1. Exponent k-values

Ce^{+3}-ions concentrations	Characteristic k-values under applied bias		
	36V	63V	90V
C_1 : 2 at.%	0.50	0.52	0.50
C_2 : 8 at.%	0.75	0.50	0.74

linear form, $LogI_{ph} = 0.59log\varphi$. The exponent k-values determine the mode of carrier recombinations whether monomolecular i.e current conduction by electrons in conduction band (CB) or holes in valence band (VB) only or bimolecular i.e. current conduction through electron-holes recombination in the material. The distinction can be observed from the relation [9]

$g = C [\Delta n^2 + 2n_0 \Delta n]$ (2)

where g represents the carrier generation rate, Δn is the excess carrier density, n_0 is the density of thermally generated carriers and C the capture coefficient at the traps. For bimolecular carrier recombination process, Δn >>n0 for which the relation (2) becomes

$\Delta n = \sqrt{\frac{g}{C}}$ i.e. $\Delta n \propto \varphi^k$ (3)

as g is proportional to φ, and k = ½ or 0.50,experimentally for all the films of different doping concentrations under different ambient conditions with white light illuminations, the average value of k remains practically constant at an average value of 0.59. This implies that the transit times of the photo-generated carriers in the host materials do not have any significant changes within the range of the applied bias and temperatures. Therefore, the bimolecular recombination (*recombination of holes and electrons from* VB *to* CB*)* process predominates the photoconduction mechanism in these films [10,11]. Such types of independence of the exponent k on applied bias and ambient temperatures is also in conformity with the observations of others [12,13]. The curves of the figure 3 show that the photocurrent *(I_{ph}= I_L-I_D)* increases with increase of φ, AB and CIs.

Characteristics of photosensitivity

From technological aspects, investigation of the properties of photosensitivity of the grown BaS samples is one of the important photoresponse parameters. Photosensitivity (S) of a material is the ratio of photocurrent to the dark current and expressed as

$S = I_{ph} / I_D$ (4)

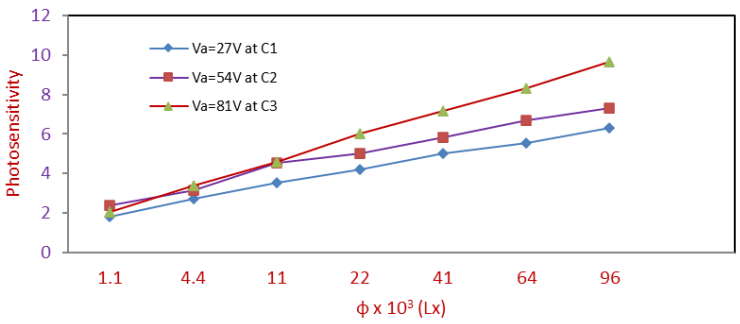

Fig.4. Photosensitivity vs. W.L. Intensity in BaS films :C_1=2at.%, C_2 = 8at.%, C_3 = 10at.% under different bias.

The Fig. 4 shows the variation of photosensitivity in the material under different excitation of WL intensity and ABs for selected samples C_1, C_2 and C_3 . It is observed that photosensitivity in these films increase with increase of intensity of WL and AB. This may be explained that as the intensity of incident light increases, the rate of generation of photocarriers also increase leading to higher concentration of free carriers (*electrons and holes*) within the material, which enhances the electrical conductivity. As more charge carriers are available to participate in the conduction process, photosensitivity increases.

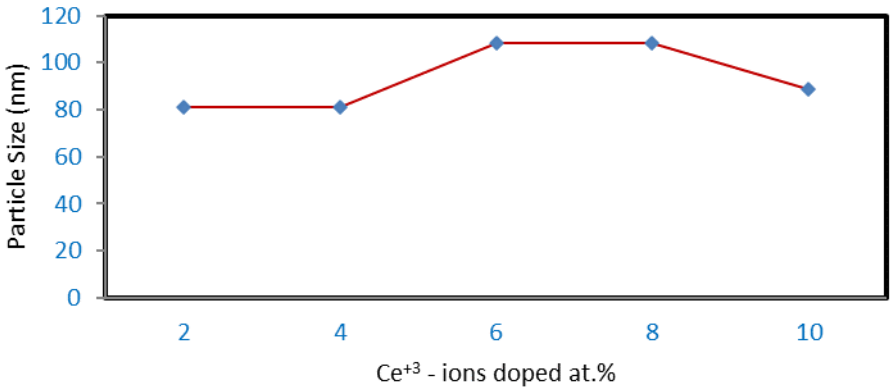

Fig.5. Particle size dependent on dosemetry plot in BaS thin films.

Fig. 5. Shows the relative change in particle size with the concentration of Ce^{+3}- ions in the BaS doped films. The detail surface morphology and X-ray diffraction spectral analysis of the samples were reported in our ealier paper [14].

IV. Conclusion

SILAR technique is found one of the best synthesis methods in synthesis of nano crystallint thin films from economic and less time points of view both in doped and undoped films. The thin films-electrodes junctions are found to be fairly ohmic for photoconductivity measurements. The photocurrents and photosensitivity in the films are found to be sublinear with the intensity of the incident white photons and the transitions of carriers are controlled by bimolecular recombination of carriers.

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