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BAND GAP SHIFT AND OPTICAL CHARACTERIZATION OF PVA-CAPPED PbO THIN FILMS: EFFECT OF THERMAL ANNEALING

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Chemical bath deposition of semiconductor nanocrystalline thin films has been carried out within the pores of polyvinyl alcohol (PVA) at room temperature. The chemical bath for the deposition of PbO is made up of lead acetate ($Pb(CH_3COO)_2$), ammonia (NH_3) and PVA solution. One of the deposited films was annealed in the oven at a temperature of 100°C and characterized for the structural and optical properties. These properties were studied by means of X-ray diffraction and optical spectrophotometer. The films' composition was determined by means of Rutherford backscattering. XRD studies revealed the formation of nanocrystalline thin films. From the absorption spectra, the band gap energy for PbO thin films lie in the range of 1.10 – 1.30eV.

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Keywords: CBD, optical properties, PbO, thermal annealing

1. Introduction

The chemical bath deposition (CBD) method has become very popular in recent time especially for thin film deposition, due to its low cost since no expensive and sophisticated vacuum equipments are required, easy process of complex shaped substrates and possibility of using high purity starting materials.

The theory behind chemical bath deposition (CBD) is quite simple and has been reported elsewhere [1, 2].

The CBD method, being less expensive than other thin film deposition methods, allows for the manufacture of relatively low cost devices, especially light detectors and light energy conversion cells. Some attempts were made to obtain binary oxides using the CBD method [2, 3], for efficient solar energy conversion through photo-electrochemical solar cells. In order to achieve high-efficiency solar cells, post deposition treatments of thin film material in air or oxygen is required, to optimise their photovoltaic performance [4]. In this paper the effect of post deposition annealing on the optical and solid-state properties of PbO thin films grown onto glass substrate using chemical bath deposition technique are reported.

2. Experimental details

It is usual in the chemical bath deposition technique for the substrates to be subjected to distinct pre-treatment to ensure the presence of catalytic surface to improve the adhesion of the films to the substrates particularly as film thickness increases. Glass microscope slides were cleaned by degreasing them in concentrated hydrochloric acid for 4 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 50°C.

First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA $(-C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at 90°C for 1hour. The temperature of the solution was allowed to drop to room temperature. Bath constituents for

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deposition of PbO thin films were lead acetate ($Pb(CH_3COO)_2$) as a source of Pb^{2+}, ammonia (NH_3) as the complexing agent in a PVA medium. To obtain deposition of PbO thin films, the chemical bath was composed of 10ml of 1M $Pb(CH_3COO)_2$, 40ml of PVA solution and 6ml of NH_3 put in that order into 50ml beaker. Clean microslide was then inserted vertically through synthetic foam into the mixture. The deposition was allowed to proceed at room temperature for 8 hours after which the coated substrate was removed, washed well with distilled water and allowed to dry.

The step-wise reaction involved in the complex ion formation and film deposition processes are given below.

$$2NH_3 + 2H2O \leftrightarrow 2NH_4OH$$

$$Pb(CH_3COO)_2 + 2NH_4OH \leftrightarrow Pb(OH)_2 + 2[NH_4CHCOO]$$

$$Pb(OH)_2 \leftrightarrow PbO + H_2O$$

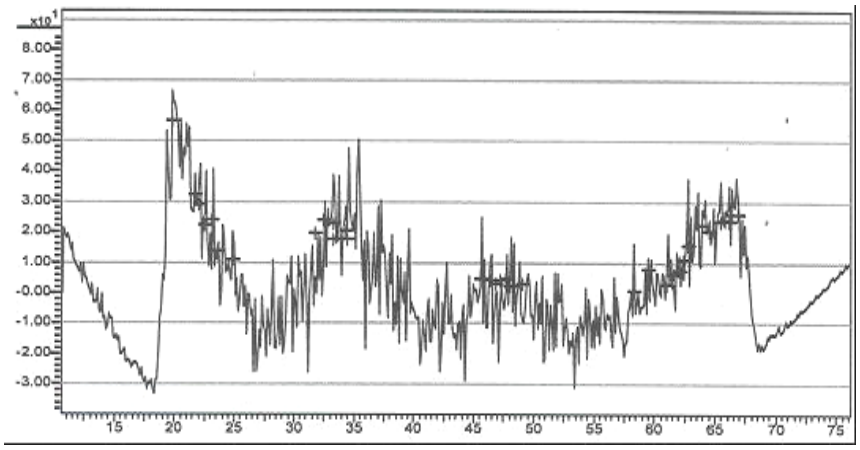
One of the deposited films was annealed in air at 100°C for one hour and labelled R9. The second sample (labelled R8) was left unannealed and used as control in order to study the effect of thermal annealing on the deposited films.

The samples were characterized with XRD, RBS and UV-VIS Spectrophotometer. Optical properties of chemical bath deposited PVA-capped PbO thin films were measured at room temperature from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1100nm. Optical band-gaps of the samples were calculated from the absorption spectra. The structure of the film was studied using X-ray diffractometer. The composition of the films was determined by using Rutherford back scattering.

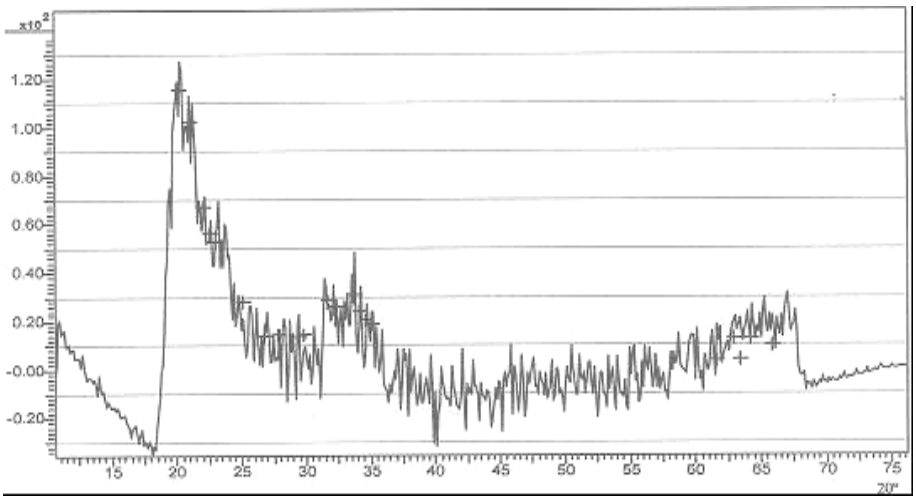
3. Results and discussion

X-ray diffraction (XRD) is an efficient tool for the structural analysis of crystalline materials. For the case of PbO thin film deposited in this work, the XRD studies was carried out on the deposited PbO films using Philips PW 1500 XRD at Engineering Materials Development Institute (EMDI) Akure, Nigeria. The result is presented in figure 1. The pattern for the thin film of PbO displayed diffraction peaks at 2θ values of approximately 19.83^0, 21.66^0, 34.40^0 and 62.72^0. The existence of identifiable peaks in the diffractograms suggests that the films are not amorphous but crystalline in nature. A close observation of figure 1 shows that thermal annealing increases the crystallinity of the deposited thin film.

The low intensity peaks observed in the XRD pattern of the sample under study shows that the films are coarsely fine crystallites or nanocrystalline. The broad hump (noise) in the displayed pattern is due to the amorphous glass substrate and also possibly due to some amorphous phase present in the PbO thin films.



(a) As-deposited PbO



(b) PbO annealed at 400°C

Fig.1: XRD pattern of PbO thin films

The grain size (D) of the films under study was determined by measuring the full width at half maximum (β) using the Scherrer formula

$$D = k\lambda / \beta\cos\theta,$$

where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54Å) and θ is the Bragg's angle. Using Scherrer's formula, the grain size was found to be of the order of 59.98nm for PbO thin films.

The elemental composition and chemical states of a sample of PbO deposited in this work and annealed at 100°C was analyzed using Rutherford Backscattering (RSB). The RBS analysis was carried out using 2.20 MeV 4He+ ions and 5.00 μC at 16.20 nA. The results are presented in fig.2. From the film composition presented in fig. 2, we can deduce that sample R9 comprises of Pb and O.

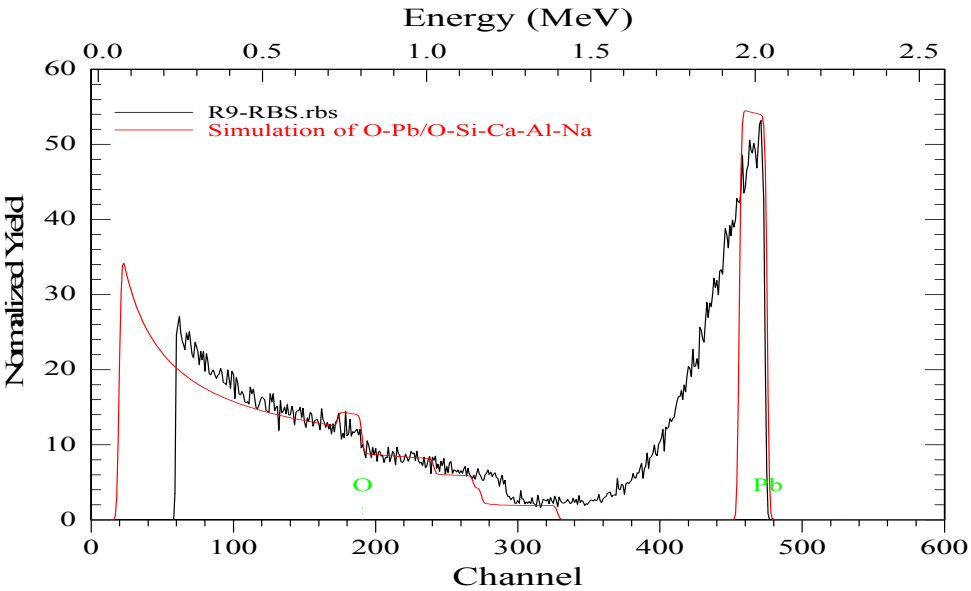


Fig 2: The RBS of PbO thin film annealed at 100°C

The optical absorption spectra of the films deposited onto glass substrate were studied in the wavelengths range of 200 – 1100nm. The variation of absorbance with wavelength for the samples annealed at 100°C and the as-grown film are shown in figure 3.

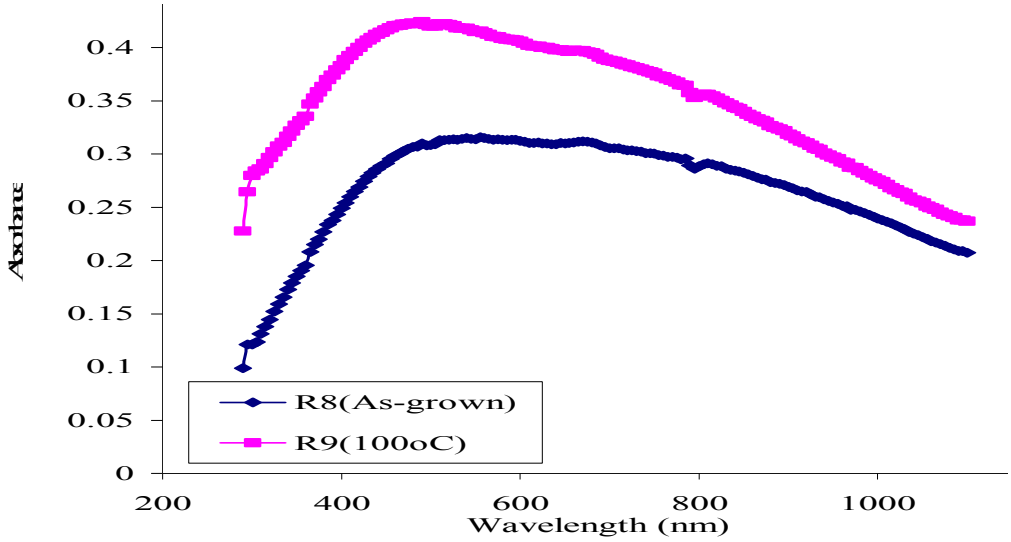


Fig. 3: Plot of absorbance vs. wavelength for PbO thin films

Figure 3 shows that the percentage absorption of solar light energy by thin films of PbO is less than 50% in all three spectra (UV-VIS-NIR) under investigation. The highest absorbance of about 45% was recorded in the visible region of the solar spectrum. The figure shows similar trend in the absorbance of the films as wavelength increases, with the unannealed film having lower absorbance value through out the entire wavelength under study.

The spectral dependence of transmittance as a function of wavelength for as-grown and annealed PbO thin films is displayed in figure 4. We observe that thin film of PbO transmits well in both the VIS and NIR spectra. It can be seen that the annealed film has the least transmittance in both the VIS and NIR spectra. The decrease in the transmittance with annealing temperature may have been caused by a decrease in the number of defects in the film. By filling the voids in the film one expects denser films and hence a decrease in the transmittance of the films. Human eye is sensitive only to the range 400 – 700nm and is peaked at 500nm [5]. This is an important factor in window coatings but is not met in the annealed film. The film however showed poor transmittance in the visible region, making it unsuitable for this purpose.

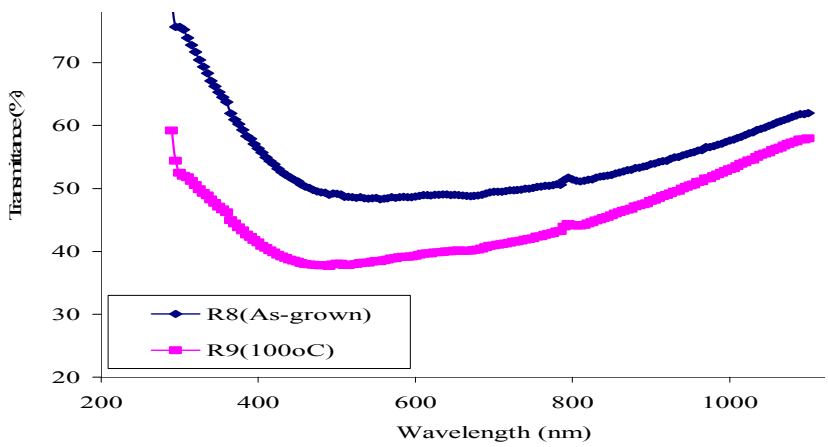


Fig. 4: Plot of transmittance vs. wavelength for PbO thin films

Figure 5 shows the spectral reflectance against wavelength for the samples under study. It can be observed in PbO thin films that the recorded reflectance is less that 25%. It can be seen from figure 5 that the reflectance increases with the annealing temperature.

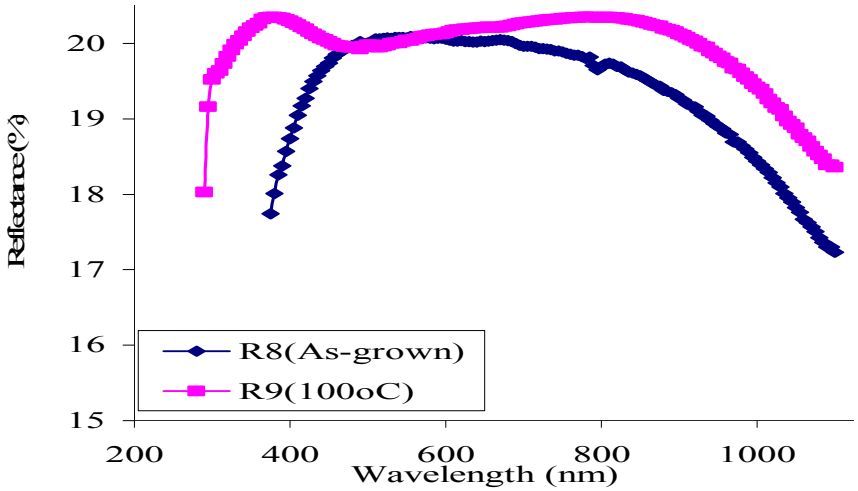


Fig. 5: Plot of reflectance vs. wavelength for PbO thin films

Thin films with high transmittance and low reflectance are good material for antireflection coatings of solar thermal devices. It has been shown that high transmittance and low reflectance properties of thin films in the visible region are the desired properties for their application in solar thermal control coatings [6]. The application of solar energy as a source of heat in chick brooding requires thin films with high transmittance in the NIR with moderate reflectance. The property of high transmittance in the NIR exhibited by these films therefore makes them good materials for use in the construction of poultry roofs and walls. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation.

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [7] while the plots of absorption coefficient against photon energy is shown in fig. 6

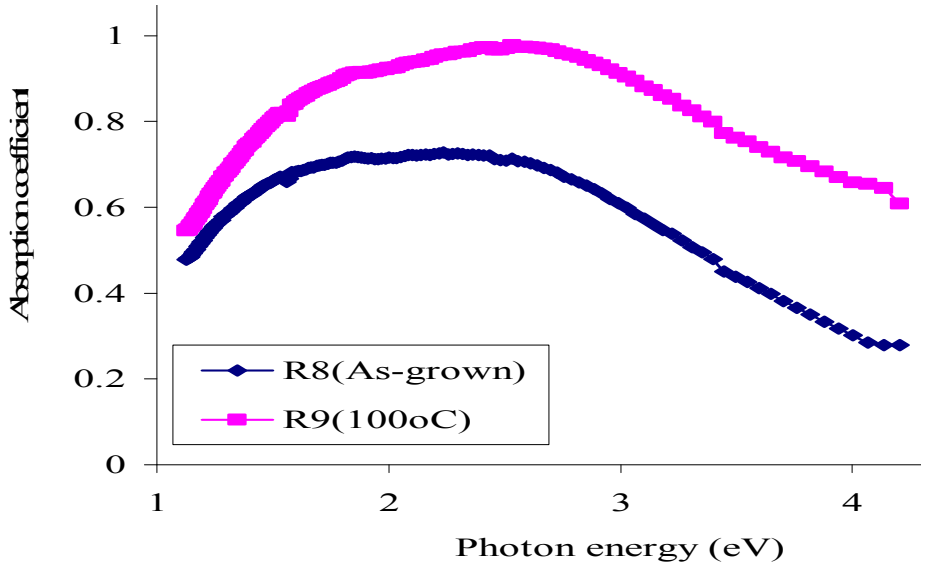


Fig.6: Plot of absorption coefficient against photon energy.

The energy band gap (E_g) for the films deposited in this work was calculated using Tauc's relation [8, 9]: $\alpha = A(h\nu - E_g)^n / h\nu$,
Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively. The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n = ½.

The values obtain for PbO thin film are 1.3eV and 1.1eV for the as-grown film and the film annealed at 100°C respectively. These values are less than the values we reported earlier for PVP-capped PbO nanocrystalline thin films [2]. A close observation of figure 7 shows that the energy gap decreased with annealing temperature. This is possibly due to the decrease in the number of defects, evaporation of water molecules off the film and reorganization of the films. The temperature dependence parameters that affect the band gap are reorganization of the film, change in the crystallite size of the film and self-oxidation [10].

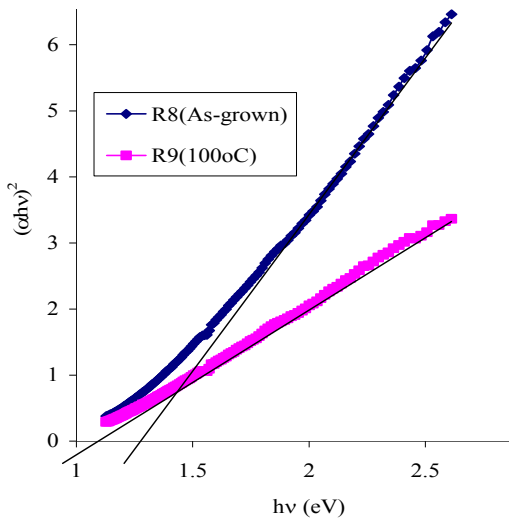


Fig. 7: $(\alpha h\nu)^2$ vs. hν for PbO thin films

A material with a direct band gap lower than 1.9eV has been regarded as a promising absorber for thin film photovoltaic applications. Higher band gap value semiconductors are used as window layer in fabrication of solar cell. The low band gap values exhibited by PbO thin film deposited in this work together with high absorption coefficient exhibited by the annealed film is an indication that PbO thin films synthesized by chemical bath deposition technique and annealed in the oven can be potentially applied as absorber material in solar cell fabrication.

Table 1 gives the average values of refractive index (n), extinction coefficient (k), real (ε_r) and imaginary (ε_i) dielectric constant of PbO thin films under study. The graphs showing how these parameters vary with photon energy are displayed in figs. 8 – 11

Table 1: Average values of refractive index (n), extinction coefficient (k), real (ε_r) and imaginary (ε_i) dielectric constant

	Refractive index	Extinction coefficient	Real dielectric constant	Imaginary dielectric constant
R8	2.16	34.07	4.65	148.51
R9	2.25	43.11	5.04	193.60

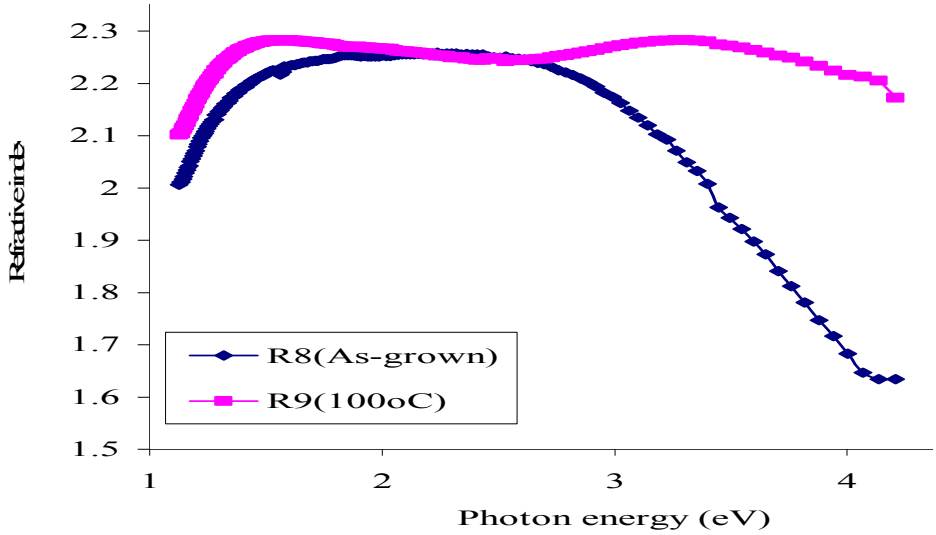


Fig. 8: Refractive index vs. photon energy for PbO thin films

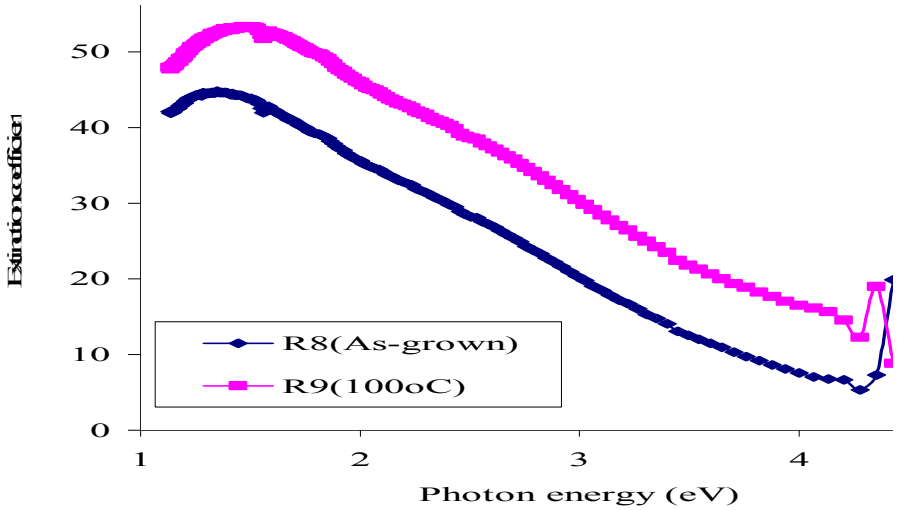


Fig.9: Extinction coefficient vs. photon energy for PbO thin films

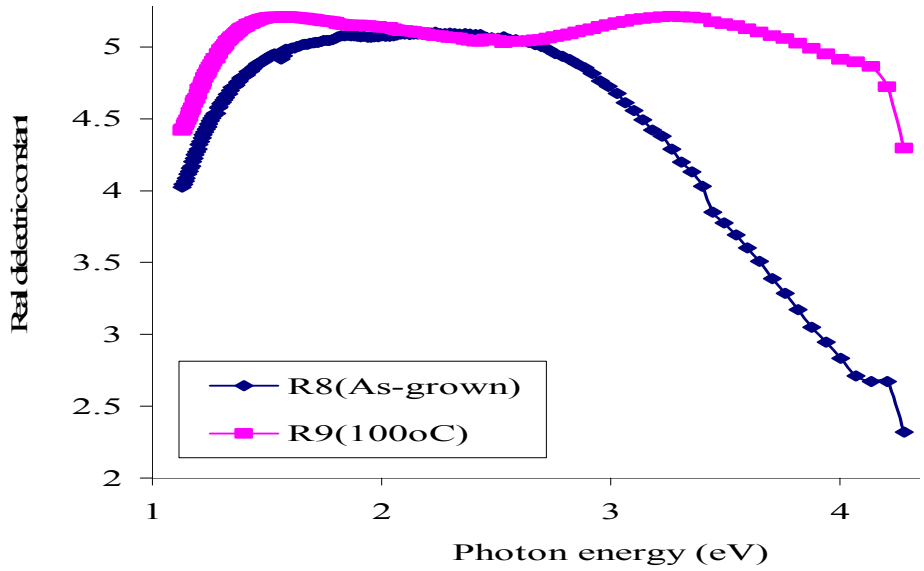


Fig.10: Real dielectric constant vs. photon energy for PbO thin films

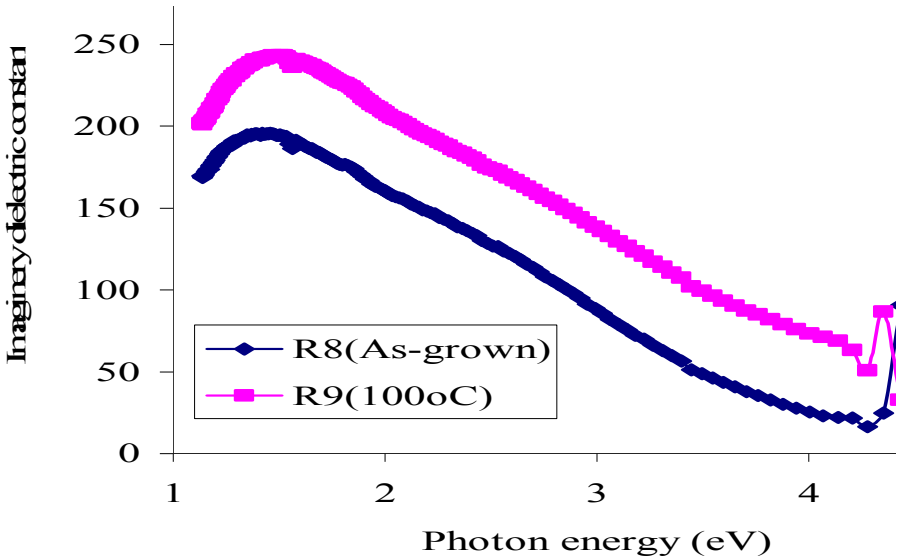


Fig.11: Imaginary dielectric constant vs. photon energy for PbO thin films

4. Conclusion

This study focuses on the synthesis and characterization of thin film materials for possible application in solar cell architecture. The films were deposited by chemical bath deposition technique. XRD study reveals better crystallization of the films when annealed in the oven at 100°C. Optical studies and band gap analysis show that thermal annealing has significant effect on these properties. The band gap energy shifts to lower value as a result of thermal annealing. The varied band gap energy exhibited by the films reported here suggests that thin film solar cell architecture could be fabricated, based on PbO thin film absorber layer.

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