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Bismuth Sulphide Thin Films by Chemical Deposition for Photoconductivity Application

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Abstract: Chemical bath deposition technique for obtaining photoconductivity Bismuth Sulphide (Bi_2S_3) thin films of thickness of about 0.07-0.19 μm is reported. At room temperature, the deposition ranges from 1-7.5 h beyond which the films start to detach from the substrate. These films show a change in dark resistance of 0.2 mΩ for a change of 0.12 μm in thickness. The dark conductivity of the film increased by a factor of 3 when annealed at 150°C for 2 h. The films showed a photo current to dark current ratio of 75-150 for the as-prepared film under 1 kWm^{-2} tungsten halogen illumination. These results suggest that post deposited annealing will enhance the performance of the films in the area of optoelectronic applications.

Key words: Bismuth sulphide thin film, chemical bath deposition, annealing, conductivity enhancement

INTRODUCTION

Photoconductivity in Bismuth Sulphide (Bi_2S_3) was earlier reported by many workers including Nair and Nair (1990), based on studies on mineral samples of bismuthinite or bismuth glance. This ascribes to bismuth sulphide the status of one of the earliest photoconducting materials. Detailed chemical deposition of these film from bismuth nitrate solution in Triethanolamine and thioureo was also described by Nair and Nair (1990). The major problem in the deposition (Nair *et al*., 1991; Kazmerski, 1980) has beenthe detachment of the films from glass substrate at durations of deposition of time greater than 7 h at 25°C, which corresponds to a film thickness of about 0.16 μm. A greater film thickness has been obtained in a double-dip deposition, in which the substrate after deposition of a thin film grown up to terminal thickness is transferred to a fresh solution for further deposition (Nair and Nair, 1992). The ease with which chemically deposited bismuth sulphide thin film can be obtained is illustrated in this research. The photoconductivity characteristics of these films are also presented.

MATERIALS AND METHODS

The procedure in the deposition of metal sulphide films by chemical bath deposited has been described in previous studies. The first problem to be tackled in the chemical bath deposition of bismuth sulphide film is the preparation of Bi^{3+} solution. The salts of Bi (III) bydrolyse in water giving rise to curdy suspensions of oxosalts. For example, the usually used bismuth nitrate, Bi $(NO_3).5H_2O$, curdles in water through the formation of oxonitrate. Bismuth salt can however, be dissolved directly in TEA as suggested by Nair and Nair (1990). The Bi_2S_3 films in the present research were prepared from bath containing 6 mL of 0.5 M solution of Bi^{3+} (prepared by dissolving 24.25 g of the bismuth salt in 72 mL of 50% TEA and made up to 100 mL with water) 2.5 mL of IM TA and distilled water to make up to 50 mL. The deposition were made on vertically supported glass slides placed inside 50 mL beaker containing the deposition mixture at room temperature (28°C) without stirring. The pH of initial bath was 8.2. The duration of deposition extended up to 6 h at room temperature and the bath became virtually depleted of constituent ions. During this period of deposition it was found that the film grew to 0.18 μm as determined by gravimetric estimation using known density of Bi_2S_3 7.4×10^3 kg m^3. It was observed that beyond 7.5 h in the bath the films started to detach from the substrate. Thicker films however, can be produced as described earlier by using double-dip deposition by transferring the film to a fresh bath.

The films after removing from the bath were flushed in distilled water and dried using a hot air dryer. Newtons ring experiment was carried out to ascertain uniformity on each workable film. The films appear golden in reflective light at lower film thickness of 0.07 μm and dark brown at

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Table 1: Details of chemical bath deposition of Bismuth sulphide thin films: Temperature and duration of deposition appearance of film and approximate film thickness as estimated by gravimetry

	Time				
Sample	h	Min.	Temperature (°C)	Appearance of film in reflected daylight	Thickness (μm)
E	1	30	28	Golden	0.07
F	3	30	0.28	Purple-golden	0.09
G	4	30	28	Dark purple	0.14
H	7	00	28	Dark brown	0.19

about 0.19 μm film thickness as described in Table 1. In order to record the variation of film resistance, conducting silver paste paint was used to form copper electrodes 2 cm apart on the film. Under a 1 kWm^{-2} Halogen lamp the variation in resistance was recorded using a digital multimeter (Becham Industrial DM 25 × L). In order to record the photo-current response, the specimen was provided with copper electrodes and placed under 1 kWm^{-2} halogen lamp. A bias voltage of 10 V for the samples was supplied from an I.C. regulated variable power supply while the current flowing was measured with a digital D.C. microameter. The photo current response curves for the samples were recorded during a 450 sec period: 100 sec dark 200 sec under illumination and 150 sec in darkness.

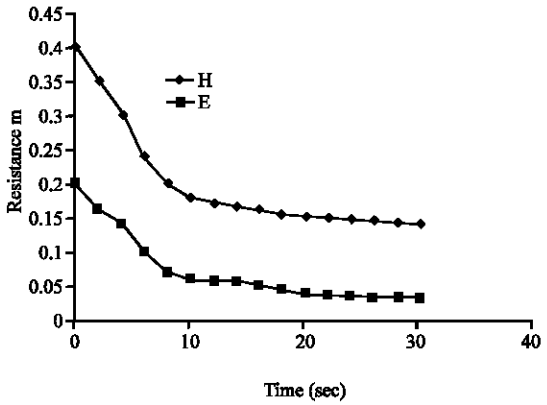

Fig. 1: Resistivity with time of samples E and H under a 1 kWm^{-2} tungsten halogen illumination

RESULTS AND DISCUSSION

The deposition of bismuth sulphide thin films seems to follow the basic mechanisms in chemical bath deposition of thin films a nucleation phase in which a hydroxide layer is deposited on the glass substrate, a growth phase which is initiated through the reaction.

$2Bi(OH)_3 + 3S^{2-} \rightarrow Bi_2S_3 + 60H^-$ and a terminal phase towards the final stages of deposition. The hydroxide phase is indicated by a smoky brownish appearance of the bath before it turns to brown and finally to dark brown.

As reported by Nair *et al.* (1991) the use of NaOH or NH_3(aq) to speed up the reaction was found to result in inferior thin films with particulate deposits on the film surface and also led to the incorporation of bismuth hydroxide into the film, giving rise to a grayish, rather than dark brown appearance of the film in reflection.

Resistivity test: Resistance variations with time under illumination was observed for photo conductivity effect. Figure 1 presents the variation of resistance with time. It is seen from the graph that there is sudden drop in resistance of the film after, which it became fairly constant.

Graph E in Fig. 1 which stands for a film of 0.07 μm thickness shows a drop from dark resistance of 0.2-0.04 mΩ in 15 sec under a 1 kwm^2 halogen lamp.

Similarly, graph H which stands for a film of 0.19 μm shows a drop from dark resistance of 0.4-0.15 mΩ is 15 sec under a 1kwm^2 halogen lamp.

This observation implies that there is a creation of electron-hole pair when the light is shown on the film (photon absorption), which then resulted in the decrease of film resistivity (i.e., an increase in conductivity). This result also, shows that the thicker the film, the higher the resistance (dark resistance-photo resistance). This is expected since the thicker film indicates the presence of more atoms which results in more electron-hole pair creation. This observation, is in agreement with the work reported by Nair and Nair (1990) and by us Fajinmi *et al.* (2001). It has been observed that the increase in conductivity with increase in film thickness is a common feature of thin films, arising from charge carrier trapping at the surface and intergrain boundaries which are thickness dependent.

Photo-current response: The photo-current response i.e., the dark current I_d, the photo-current I_{ph}, the growth and decay of the photocurrent as well as the spectral response of the photo-current in metal chalcogenide thin films such as CdS and PbS (Fajinmi *et al.*, 2001) are known to be drastically dependent on the deposition conditions and post deposition processing of the films.

Figure 2 shows the drastic effect of air annealing on the photocurrent response of bismuth sulphide film. The

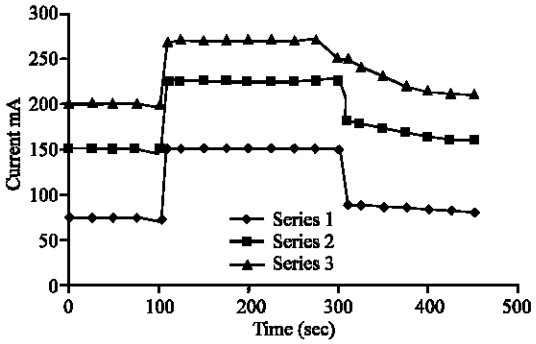

Fig. 2: Effect of air annealing on the photo-current response of sample H: 1, as prepared (bias 8 v), 2, after 1 h air annealing at 150°C (bias 1 v), 3 after 2 h air annealing at 150°C (bias 1 v)

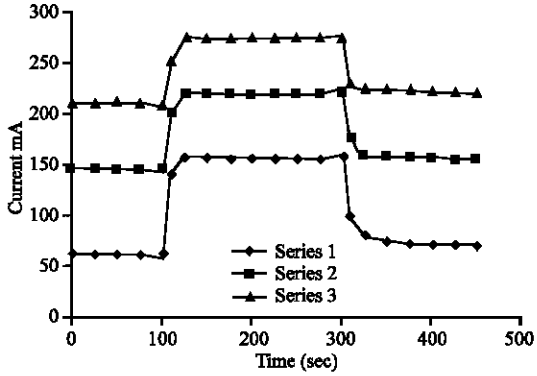

Fig. 3: Sytematic variation of the photo-current response of samples E-G after air annealing for 1 h at 150°C

dark current of the as prepared sample H is 75 mA which increased to 150 mA after 1 h annealing at temperature of 150°C and to 200 mA when annealed for 2 h at temperature of 150°C. It is also, observed that the dark to photo current ratio for the as prepared is greater than that of annealed. It is seen that the photo-current decay is slower in the annealed sample than the as prepared. This may be as a result of the radiation in trapping mechanism during annealing. This is in accordance with our earlier result on PbS (Fajinmi, 2001). Figure 3 shows the systematic variation in the photo-current response of sample E- G of Table 1 after annealing for 1 h at 150°C.

There is considerable increase in photo and dark current values with increase in film thickness. For example, it is observed that the steady state dark and photo current in sample E after 1 h annealing at 150°C are 62 and 150 mA, respectively and the corresponding values in sample G are 210 and 275 mA, respectively, showing an increase in dark and photocurrent values of a factor of about 130 mA while the film thickness has increased only by a factor of 0.07 μm Such increase in photo and dark conductivities with increase in film thickness <1 um can arise from the enhancement of charge carrier mobility and or the photocarrier lifetime.

Variation of the photo and dark conductivities upon annealing may also involve processes like amorphous to crystalline transition, changes in micro-crystallinity including modification of intergrain boundries[1] Preliminary X-ray studies carried out (Nair *et al.*, 1991) showed that the as prepared Bi_2S_3 films are amorphous and with air annealing made at increasing temperatures up to 200°C crystallinity is brought into the film.

CONCLUSION

The Bismuth sulphide films are found to be photoconductive with photo to dark current ratio of about 40-80 when measure at 28°C under a 1 kWm^{-2} tungsten halogen radiation (Fig. 2).

It was also, shown in Fig. 2 and 3 that post deposition annealing can have remarkable effect on the optoelectronic properties of these films. Figure 3 shows that there is an increase in photo and dark current values with an increase in film thickness. The results as presented in this study have led to considering chemically deposited Bismuth Sulphide thin films potentially important for photoconductive and photovoltaic application.

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