Bias-induced changes in carrier type of $Pb(i\_{x})Fe_{(x)}S$ nanocrystalline solution grown thin films

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Abstract

Change of majority carrier type was achieved in nanocrystalline $Pb(i\_{x})Fe(_{x})S$ thin films by applying a DC-bias on the substrate during their growth by solution growth technique. Critical control of biasing and pH of the solution bath are observed to be necessary to achieve this change. The DC-bias results in slight change in relative concentrations of the constituents in the films, which lead to change in majority carriers without any measurable change in lattice parameter. This modification to the conventional solution growth technique provides the possibility to grow abrupt homojunctions in the nanocrystalline films by sudden change in DC-biasing during film growth.

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1. Introduction

Nanocrystalline thin films of ternary alloy semiconductors Pb^^Fe^S were grown for iron concentration 0:25pxp0:75 using a chemical bath deposition (CBD) technique. Critical control of growth parameters of the chemical bath like its composition, pH value and temperature was found to be necessary for the growth of good quality homogeneous films of the ternary materials. The films grow with a structure typical of PbS. The optical band gap of the film materials was observed to decrease linearly between 2.65 and 2.22 eV with increase in iron concentration from 0.25 to 0.75. FeS is known to have a band gap of 0.04 eV [1] and hence alloying of PbS with FeS is expected to decrease the band gap of the ternary alloys with increase in iron concentration in the films. Optical band gap value of 2.82 eV (extrapolated value) obtained for the PbS $(x = 0)$ material agrees with that reported for nanocrystalline PbS with grain size of B6nm [2,3].

Carrier type in PbS is known to depend on concentration of sulfur in the films; stoichiometric excess of sulfur imparts a p-type character to the films whereas films with deficient sulfur are n-type [4]. It is thus felt that if the concentration of S^{2}~

ions reaching the substrate is manipulated during growth of the ternary $Pb_{(1-x)}Fe_{(x)}S$ films, it may lead to change in their carrier type from p to n and vise versa. Such a condition could possibly be achieved by applying a positive or a negative bias to the substrate during growth of the films. It is apparent that an abrupt change in bias conditions during growth could pave way for growth of abrupt homojunctions in the films.

2. Experimental procedure

In the present investigations, thin films of $Pb_{(1-x)}Fe_{(x)}S$ were grown on p-type Si substrates under different bias conditions. Biasing was provided with the help of a DC power supply and a capacitor circuit. (M/25) lead acetate, (M/25) ferrous chloride and (M/20) thiourea aqueous solutions prepared from AR grade chemicals and deionized water were used for growth of ternary films with desired compositions. Chemically cleaned p-type Si substrates were dipped in the lead acetate-thiourea solution mixed in equal proportions. The chemical bath maintained at a temperature of 33 1C (7 11C) was stirred continuously. Liquor ammonia was gradually added to bring pH of the solution to 9.0. Appropriate quantity of the aqueous (M/25) ferrous chloride solution was added at this stage to obtain a particular x value in the films. Quantities of precursors to obtain specific x in the $Pb_{(1-x)}Fe_{(x)}S$ films were optimized from analysis of X-ray fluorescence spectroscopy (XRFS) data obtained from test films grown under identical conditions. pH of the bath was then driven to an optimized higher value; which was found to be a function of iron concentration in the films (Table 1). Hall effect measurements were carried out on films with equal thickness, using a model S1 10 Keithely Hall Measurement system. Gold dots were evaporated to provide ohmic contact.

Table 1
Effect of DC-bias and pH on carrier type in $Pb_{(1-x)}Fe_{(x)}S$ films

DC-bias (V)	$Pb_{(0.5)}Fe_{(0.5)}S$	$Pb_{(0.75)}Fe_{(0.25)}S$		$Pb_{(0.25)}Fe_{(0.75)}S$	
	Optimum pH				
	10.50	10.50	9.50	10.50	11.50
+45	P	P	P	n	P
+30	P	P	P	n	P
+15	P	P	P	n	n
0	P	P	P	n	n
-15	P	P	P	n	n
-30	n	P	n	n	n
-45	n	P	n	n	n

3. Results and discussion

The films grown under zero, positive and negative bias conditions were found to be homogeneous and uniform. Films with different iron concentrations (x) were grown for optimized times to obtain thickness of B 200 nm. X-ray diffraction (XRD) data obtained from films with iron concentration (x) between 0.25 and 0.75 indicate the presence of single-phase ternary materials with lattice type identical to that of PbS. Shift in XRD peaks towards larger y indicate decrease in lattice parameter with increase in iron concentration (x) (Fig. 1). XRD peaks were observed at same y values for films with a fixed x but grown under different bias conditions, indicating no measurable

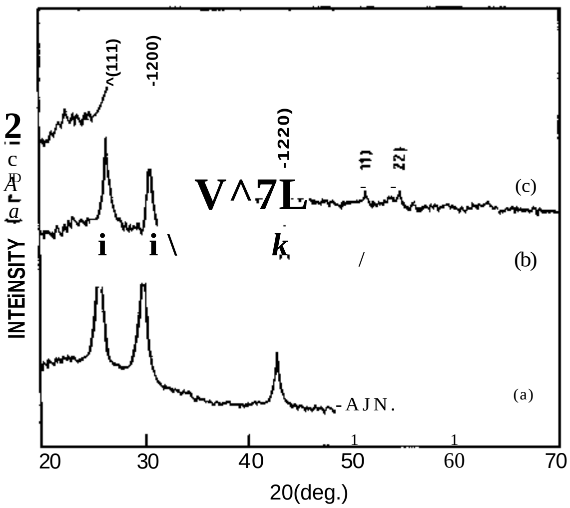

Fig. 1. XRD traces for (a) $Pb_{(0.75)}Fe_{(0.25)}S$, (b) $Pb_{(0.5)}Fe_{(0.5)}S$, and (c) $Pb_{(0.25)}Fe_{(0.75)}S$ thin films grown under zero bias condition.

Table 2
Effect of DC-bias on average grain size and relative concentrations of constituents in $Pb_{(0.5)}Fe_{(0.5)}S$ films

DC-bias (V)	Av. grain size (nm)		Concentrations (weight %)		
	TEM	XRD	Pb	Fe	S
+ 30	19	18	63.70	16.70	19.60
0	17	15	63.43	17.07	19.50
-30	14	12	62.80	18.04	18.80

change in lattice parameter with biasing of the substrate. Average grain size estimated from the transmission electron microscopy (TEM) studies indicated the presence of nanocrystal grains in the films. The grain size was observed to decrease from 23 to 11 nm with increase in iron concentration *(x)* from 0.25 to 0.75 in films grown under zero bias conditions. The grain size in the films grown with same *x* but different DC-bias was observed to decrease with increase in the negative bias. Average grain size in the films measured from TEM pictures agree well with those estimated from peak broadening in the XRD measurements using Scherer equation [5]. Results from typical films with $x = 0.50$ are summarized in Table 2.

Slight variation in relative concentrations of Pb, Fe and S was observed in films grown under different bias conditions. XRFS results carried out on films grown under different bias conditions indicate that for positive DC-bias weight percentage of Pb and S slightly increase whereas that of iron slightly decreases in comparison to those in the films grown at zero bias. On the other hand, under negative bias, the Pb and S concentrations (weight percentage) slightly decreased and the iron concentration increased over those in films grown at zero bias. Typical results from films with $x = 0.50$ are presented in Table 2. It was possible to enhance this effect by changing pH of the solutions which controls availability of S^{2-} ions produced by hydrolysis of thiourea in the basic medium.

Hall effect measurements indicate that the films grown under pH of 10.5 and no bias ($V_0 = 0$) condition are p-type for $0.25 \leq x \leq 0.50$ and n-type for $x = 0.75$. Films with iron concentration $x = 0.50$ were observed to grow in a bath with pH of 10.5 as p-type under V_0 of $+45\,V \geq V_0 \geq -15\,V$ and as n-type under V_0 of $-30\,V \geq V_0 \geq -45\,V$. The $x = 0.25$ films grown in pH of 10.5 and V_0 of $+45\,V \geq V_0 \geq -45\,V$ grow as p-type. However, on reducing pH to 9.5 the films grow as p-type in the range $+30\,V \geq V_0 \geq -15\,V$ and as n-type for $V_0 \leq -30\,V$. Films with iron concentration $x = 0.75$ grown at pH of 10.5 were n-type in the range $+45\,V \geq V_0 \geq -45\,V$. However, when the pH was increased to 11.5 the films were n-type in the range $+15\,V \geq V_0 \geq -30\,V$ and p-type for $+45\,V \geq V_0 \geq +30\,V$. The results are summarized in Table 1.

4. Conclusions

Investigations reported in this paper indicate that appropriate control on pH of the chemical bath and biasing potential of the substrate lead to change in carrier type in the nanocrystalline $Pb_{(1-x)}Fe_{(x)}S$ films with no measurable change in lattice parameter of the film materials. The change in carrier type is brought about by exercising control on relative availability of cationic and anionic species on the substrate during growth of the film. The technique thus provides a simple but effective method for in situ growth of homojunctions in polycrystalline and epitaxial films of binary and ternary semiconductors. Biasing of the substrate to achieve change in carrier type is likely to be effective also in films of binary and ternary chalcogenide semiconductors grown by the plasma CVD techniques.

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