Change of majority carrier type in PbS nanoparticle films

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Received 18 June 2004; accepted 29 June 2004

Abstract

Change of majority carrier type from p to n in PbS semiconductor nanoparticle films grown from a solution bath has been achieved by applying an appropriate negative DC-bias to substrate during growth. This change is attributed to the observed decrease of sulfur content in the films which is accompanied by reduction in grain size on increasing the negative bias applied to the substrate.

Pacs: 81.05.Hd; 73.61.Tm

Keywords: Solution growth; Nanoparticles; Lead sulfide; Carrier type

1. Introduction

Lead sulphide (PbS) has been projected as a material of interest to study the quantum size effect in recent years [1-3]. Structural, optical and electrical properties of PbS nanoparticles have been studied extensively [4-7]. PbS in bulk form is a material of potential application for infra-red detection. However, reduction of grain size extends the employability of the material over wide spectral range. Considering the fact that stoichiometric excess of sulfur in PbS (bulk) imparts p-type character whereas deficient sulfur makes it n-type [8], a similar change in carrier type can be expected in PbS films by manipulating the sulfur content. In chemical bath deposition technique, which has been used for the growth of PbS films for the present study, the stoichiometry is determined by the relative availability of the ions reaching the substrate to undergo reactions at the surface. A change, intentional or otherwise, in relative concentrations of the ions reaching the substrate surface can lead to non-stoichiometry in the resulting films. It is thus possible to grow films with excess or deficit sulfur by modifying its supply to the substrate during growth of films. The modified solution growth technique which has been used to change the carrier type in ternary
Pb$_{1-x}$Fe$_x$S nanoparticle films [9] by applying an appropriate DC-bias to the substrate during growth of film is used for a well-known binary semiconductor, PbS, nanoparticle films. We have reported that an appropriate choice of DC-bias to the substrate could modify availability of sulfur ions at the surface and observed that a positive bias enhances and a negative bias impairs relative supply of sulfur ions to the substrate during the growth of Pb$_{1-x}$Fe$_x$S films. The successful fabrication of homojunctions between the nanoparticle films indicates the reliability of the technique [10]. In this letter, we have made an attempt to use the technique for PbS films. Effect of DC-bias applied to the substrate during growth on average grain size and carrier type of films is discussed.

2. Experimental

Nanoparticle films of PbS were grown on p-type silicon (Si) substrates from an alkaline chemical bath. M/40 lead acetate and M/30 thiourea were mixed in equal proportions. Initially, cleaned substrates were dipped in the solution. The chemical bath was maintained at a temperature = 35 $^\circ$C and pH = 10.25 and solution was stirred continuously. Thin films of PbS were grown on p-Si substrates under different biasing conditions. Biasing was provided with the help of a DC-power supply and capacitor circuit. Films were grown for an optimized time to achieve a thickness of 150 nm. Average grain size in films is estimated by transmission electron microscopy (TEM) which is discussed elsewhere [7]. Hall effect measurements (S1 10 Keithely Hall measurement system) were carried out in order to study the carrier type in films using ohmic electrical contacts and an spectro X-Lab 2000 energy dispersive X-ray fluorescence (EDXRFS) was used for chemical analysis of the films.

3. Results and discussion

Maximum thickness limit of the PbS films obtained from a single growth step known as terminal thickness of the films was observed to decrease with increase in negative bias. The PbS nanoparticle films grown under zero and positive biasing are observed to have FCC structure. The grain size estimated by TEM studies and the peak broadening in X-ray diffraction patterns for films shows a decrease with decrease of DC-bias from positive to negative through zero applied to the substrate. Fig. 1 clearly shows the decrease in average grain size with a decrease of DC-bias applied to the substrate. Fig. 2 shows the linear dependence of average grain size on DC-bias applied to the substrate. Similar kind of decrease of grain size with negative bias was observed by the authors in Pb$_{1-x}$Fe$_x$S ternary nanoparticle films [9]. The Hall effect studies carried out on PbS semiconductor nanoparticle films show a change in majority carrier type. Films are found to be p-type for the DC-bias of more than $-24$ V whereas grown as n-type for a DC-bias of $-36$, $-48$ and $-60$ V. The results are summarized in Table 1. The observed change of carrier type at higher negative DC-bias values associated with a decrease of grain

![Fig. 1. TEM micrographs for PbS nanoparticle films grown at DC-bias of (a) + 12V, (b)-24 V, (c) -60V.](image-url)
size in nanometer range in the films can be attributed to the decrease of sulfur content in the films with decrease in size. The decrease of sulfur in films was confirmed from the EDXRFS data obtained for the PbS films. The EDXRFS results suggest the chemical compositions like PbS1.08, PbS0.987, and PbS0.981 for films grown under DC-bias of +12, —36 and —60 V, respectively. This is to mention that no measurable change was noticed in the Pb content in the films grown with a given range of positive DC-bias being applied to the substrate. It is thus believed that the negative bias applied to the substrate is offering a repelling force to negatively charged $S^{2-}$ ions in the solution at the vicinity of the substrate which leads to the growth of sulfur-deficient films. It is also interesting to note that the carrier type in the PbS films grown under DC-biased condition is found to be a function of the average grain size. Therefore, it is of worth to mention the work done by Balamurugan et al. [11] and Xiong et al. [12] in the context of size and stoichiometric-dependent carrier type in semiconductor films, respectively. Balamurugan et al. have achieved a change of carrier type from p to n in Cu$_2$O nanoparticle films with reduction of grain size which was attributed to the change in position of fermi level with particle size. Xiong et al. reported the formation of n- and p-type ZnO films by deposition of the layers under oxygen-poor and oxygen-rich conditions to manipulate the stoichiometry by a reactive sputtering technique. Considering the reliability, simplicity and availability it can be concluded that our method of manipulating the stoichiometry which has already been used for ternary films is more practical and established than the method reported by Xiong et al.

4. Conclusions

Modified solution growth technique has been successfully implemented to achieve an inversion of carrier type in a well-known semiconductor (PbS) by manipulating the stoichiometry. This method is likely to be useful for other binary and ternary chalcogenides by appropriate selection of precursors and DC-bias.

References