Chapter 7

Electron spin resonance (ESR) of PbS:Ag nanorods

7.1. Introduction

Creation of paramagnetic centers in semiconductors is of great fundamental interest over the years and has led to many exciting findings in Physics. Although paramagnetic ion doping in various II-VI and IV-VI semiconductors has been studied [129-131], creation of Ag paramagnetic centers and determination of their valence state in PbS (galena) are scarcely addressed [132]. The occurrence of pure metallic silver in galena is also very rare in nature. Simple substitution of Ag$^+$ in PbS (2Ag$^+$=Pb$^{2+}$) through solid-state reaction is limited to only 0.4 mol% at 615$^\circ$C [133,134]. The diffusion coefficient of silver in PbS is found to be very low ~ $10^{-10}$ cm$^2$/s at 500 $^\circ$C [135]. It is further observed that the silver uptake in PbS can be enhanced when substitution takes place accompanying other ions (Sb, Bi etc.), like Ag$^+$ + Sb$^{3+}$=2Pb$^{2+}$ forming diaphorite Pb$_2$Ag$_3$Sb$_3$S$_8$. The insolubility of Ag in PbS arises out of the fact that half of the silver atoms are isomorphically substituted in the interstitial site in PbS. Such a structural configuration is energetically unfavorable for stable existence of Ag and PbS. However, the thermodynamic data reveals that there exists a wide range of temperature and $f$ values in which Ag and PbS can stably coexist [136,137].

The basic objective of this chapter is to address the structural role of Ag in PbS host and their paramagnetic behaviors. We show here that in low dimensional structures of PbS, here in the form of nanorods in polymer matrix, Ag uptake in PbS can be increased to 1.76 mol%. Determination of the structural information of silver at low concentrations in presence of matrix containing heavy element Pb seems to be a challenging task. ESR is found to be quite sensitive in revealing such information for magnetic elements, even if the elemental concentrations present in the matrix is low. Interestingly, we found the valence state of silver present in PbS to be Ag$^0$ and Ag$^{2+}$. Both Ag$^0$ and Ag$^{2+}$ paramagnetic centers simultaneously coexist in PbS structure, as revealed by electron spin resonance spectrum (ESR), which are
not reported before. Creation of both the paramagnetic centers is instigated by the formation of vacancies when PbS undergoes a strain induced lattice distortion from cubic to tetragonal one, as discussed here.

7.2. Experimental

Solutions of lead nitrate and sodium thiosulfate dissolved in a mixture of ethanol and distilled water (2:1) are used as the precursors for lead and sulfur. Sulfidation takes place under rapid stirring condition when sulfur-containing solution is added to the mixture of Pb$^{2+}$ solution and polypyrrole at a temperature 70°C. Silver doping is accomplished by the replacement of Pb$^{2+}$ by 5 mol% of Ag$^+$ in the starting solutions (using silver nitrate as the precursor). Here we are concerned with four samples, S-1 to S-4.

The samples S-1 and S-2 contain PbS nanorods grown with 5 wt% of polypyrrole at 300 K, the first one is undoped and the latter being doped with silver. Samples S-3 and S-4 are silver doped grown with polypyrrole concentration 10 wt% and 15 wt % at temperature 333 K respectively. We find that dopant concentration of silver really been doped in the PbS lattice largely differs from that of silver concentration in the starting solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>Undoped PbS grown with 5 wt% of Polypyrrole at 60°C</td>
</tr>
<tr>
<td>S-2</td>
<td>0.58 mol% Ag$^+$ doped PbS grown with 5 wt% of Polypyrrole at 60°C</td>
</tr>
<tr>
<td>S-3</td>
<td>1.17 mol% Ag$^+$ doped PbS grown with 10 wt% of polypyrrole at 80°C</td>
</tr>
<tr>
<td>S-4</td>
<td>1.76 mol% Ag$^+$ doped PbS grown with 15 wt% of polypyrrole at 80°C</td>
</tr>
</tbody>
</table>
7.3. Results and discussion

The diameter (D) of nanorods (obtained from TEM) is found to increase with the increase in polymer concentrations: D=30 nm for S-1 and S-2, 50 nm for S-3 and 80 nm for S-4 respectively. A representative TEM image of sample S-4 is given in Figure 25, inset of which shows the corresponding selected area electron diffraction pattern (SAED). The diffraction spots in SAED are clear indicative of the single crystalline growth of PbS nanorods in polymer.
**Figure 25:** TEM images showing the formation of nanorods of diameter approximately 80 nm (for sample S-4). Inset shows the selected area diffraction pattern indicating single crystalline growth of nanorods.

**Figure 26:** SEM images showing the formation of nanorods.

The surface morphology of nanorods is characterized by scanning electron microscope (SEM). Figure 26 indicates the narrow size distribution of nanorod sample.
The x-ray diffraction spectra for a representative sample (5 wt% pyrrole) with different silver concentrations are given in Figure 27. Shift in peak position (hence in lattice spacing d) compared to bulk indicated a strong lattice distortion (both contraction as well as expansion). The PbS lattice loses its cubic symmetry and transforms into a tetragonal one. The same can also be observed for silver doped samples. It is also interesting to note that dopant concentration of silver in the nanorods severely dependent on their size.

![XRD spectra of PbS nanorods for undoped sample and silver-doped representative samples along with data bulk PbS.](image)

**Figure 27**: XRD spectra of PbS nanorods for undoped sample and silver-doped representative samples along with data bulk PbS.

The composition analysis of the doped sample obtained from the energy dispersive x-ray spectroscopy (EDS) profile is shown in the Figure 28. The EDS measurements are carried out at different regions of each sample are found to have uniform elemental compositions. The elemental percentage analysis obtained for samples is shown in the Table 1.
Table 1: The elemental percentage analysis of silver doped PbS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>S</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-2</td>
<td>74.58</td>
<td>22.81</td>
<td>0.58</td>
</tr>
<tr>
<td>Sample-3</td>
<td>76.02</td>
<td>22.81</td>
<td>1.17</td>
</tr>
<tr>
<td>Sample-4</td>
<td>77.32</td>
<td>20.92</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Figure 28: EDS profile showing the elemental compositions for the silver-doped samples.
The identification of Ag in PbS host and their paramagnetic behaviors is obtained through the analysis of ESR spectra given in Figure 29 for all the silver doped samples S-2, S-3 and S-4 respectively. ESR measurements are carried out at 9.833 GHz at room temperature with a Bruker BioSpin GmbH spectrometer. With a judicious choice of modulation frequency (50-100 kHz) and modulation amplitude (10-15 Gauss) ESR signals are recorded without any appreciable spurious signals.

**Figure 29:** Room temperature ESR spectra of silver-doped samples.
Figure 30: (a) fcc cubic structure of bulk PbS (b) tetragonal lattice structure with Ag\(^0\) and Ag\(^{2+}\) positions.

Figure 31: Optical absorption spectra for PbS nanorods for undoped sample and silver-doped samples. The arrow mark indicates the position of the surface Plasmon absorption band for sample S-2.
The ESR signals are assigned to either silver atom $\text{Ag}^0$ (4d$^{10}$5s$^1$) and/or $\text{Ag}^{2+}$ (4d$^9$) center ($\text{Ag}^+$ being ESR inactive). The only signal observed for sample S-2 at 3510 Gauss is assigned to $\text{Ag}^0$ atoms. To maintain the charge neutrality of the PbS structure, only $\text{Ag}^0$ centers can’t be formed inside the PbS lattice, rather they are residing at the PbS surface.

This is further confirmed by the appearance of a broad surface plasmon resonance (SPR) band at ~ 420 nm as shown by arrow mark in Figure 31.

Such SPR band appears only for sample S-2, not for samples S-3 and S-4. Adsorption of $\text{Ag}^+$ ions at the galena surface and their subsequent conversion into $\text{Ag}^0$ through ion-exchange reaction can be the plausible mechanism, as observed earlier by Scaini et al. [138].

In addition to the ESR signal for $\text{Ag}^0$, both the sample S-3 and S-4 exhibits another signal at ~ 3260 Gauss which is attributed to the $\text{Ag}^{2+}$ paramagnetic centers. Further, sample S-4 shows additional splitting of the ESR signal due to $\text{Ag}^{2+}$ centers with components asymmetrically located at ~ 3465 Gauss and 3592 Gauss respectively. Now, substitution of $\text{Pb}^{2+}$ by $\text{Ag}^+$ in the PbS lattice must be associated with the simultaneous creation of $\text{Ag}^0$ and $\text{Ag}^{2+}$ centers to maintain the cation-anion ratio and charge neutrality of the system. Creation of $\text{Pb}^{2+}$ (hole) vacancies to act as a trap of $\text{Ag}^+$ ions and subsequent conversion into $\text{Ag}^0$ and $\text{Ag}^{2+}$ centers needs to be clarified to justify the ESR result.

PbS (galena) has the fcc cubic lattice with octahedral coordination of Pb and S atoms. XRD data indicated the strain-induced distortion of the lattice gives rise to a tetragonal structure. $\text{Ag}^+$ ions are supposed to be dissolved in a substitutional way and according to the reaction:

\[
\text{substitutional ion} \rightarrow \text{interstitial ion}^+ \text{ vacancy}
\]

Silver occupies both the interstitial site as well as substitutional site of the lattice. Now the size of the substitutional $\text{Ag}^+$ ions (0.126 nm) is much smaller than the host $\text{Pb}^{2+}$ ions (1.33 nm), more than a factor of 10. The mismatch in size of the host and solute ions would therefore be expected to generate a large local strain within the lattice. This is true in both cases, whether an oversized ion replaces a smaller host ion or an undersized atom replaces a larger host ion. One would therefore expect a strain-induced binding of the $\text{Ag}^+$ ions into the cation vacancy. This large strain induced binding energy therefore lowers the activation energy of diffusion significantly and it is further decreased with the increase in temperature. The vacancy binding energy is supposed to be proportional to the size
difference of the Ag\(^{+}\) and Pb\(^{2+}\) ions. The size difference of the solute and host ions
determines the amount of strain generated on the host matrix and thereby controls the ability
of the Ag\(^{+}\) ions to capture vacancies. This explains clearly the substitution of Ag\(^{+}\) ions into
the PbS lattice for samples S-3 and S-4 which are grown at relatively higher temperature 333
K. Ag\(^{2+}\) ions are supposed to occupy the Pb\(^{2+}\) sites and Ag\(^{0}\) atoms at the interstitial site of
PbS lattice.

The Ag\(^{0}\) centers in sample S-2 responsible for the single symmetric ESR line at 3510
Gauss is characterized by \(g = 2.00234\) having narrow line-width ~ 8 Gauss respectively. The
g value ~ 2 further indicates weak spin-lattice coupling in the present system. For sample S-
2, no splitting due to hyperfine interactions with \(^{107}\)Ag (51.8\% abundance) and \(^{109}\)Ag (48.2\% abundance)
isotopes is observed (each having nuclear spin \(I=1/2\)). The nuclear gyromagnetic
ratio for \(^{107}\)Ag = 1.237 X 10\(^{-4}\) and that of for \(^{109}\)Ag = 1.422 X 10\(^{-4}\) respectively. The line-
width slightly increases to 12 Gauss for Ag\(^{0}\) centers in sample S-3 without any change in g
value. The line becomes complicated for sample S-4 with the appearance of two additional
signals asymmetrically located on either side of the main signal at ~ 3510 Gauss. These two
signals are separated by a field as large as ~ 127 Gauss. The line-width of the main signal
remains almost unchanged with respect to samples S-2 and S-3. The observation of
(moderately intense) the asymmetric doublet with large field splitting is strong indicative of
the hyperfine interactions of \(^{107}\)Ag and \(^{109}\)Ag isotopes with \(I=1/2\). The doublet can be
approximately characterized with narrow line-width same as that of the main signal (10
Gauss) and having intensity ratio consistent with that expected from the natural abundance of
two isotopes. However, it can safely be concluded that splitting of Ag\(^{0}\) inherits due to Breit-
Rabi effect [139] rather than the presence of inequivalent silver atoms in the PbS lattice.
From the Breit-Rabi theory, the spin Hamiltonian for 2S\(_{1/2}\) electronic state can be written as:

\[
H = g\beta B \cdot S + A I \cdot S
\]  \hspace{1cm} (11)

We obtained the hyperfine coupling constant \(A\sim0.3\) cm\(^{-1}\) indicating the case of strong
hyperfine coupling.