Nano sulfide and oxide semiconductors as promising materials for studies by positron annihilation

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Abstract. A number of wide band gap sulfide and oxide semiconducting nanomaterial systems were investigated using the experimental techniques of positron lifetime and coincidence Doppler broadening measurements. The results indicated several features of the nanomaterial systems, which were found strongly related to the presence of vacancy-type defects and their clusters. Quantum confinement effects were displayed in these studies as remarkable changes in the positron lifetimes and the lineshape parameters around the same grain sizes below which characteristic blue shifts were observed in the optical absorption spectra. Considerable enhancement in the band gap and significant rise of the positron lifetimes were found occurring when the particle sizes were reduced to very low sizes. The results of doping or substitutions by other cations in semiconductor nanosystems were also interesting. Variously heat-treated TiO$_2$ nanoparticles were studied recently and change of positron annihilation parameters across the anatase to rutile structural transition are carefully analyzed. Preliminary results of positron annihilation studies on Eu-doped CeO nanoparticles are also presented.

1. Introduction

Several of the physical properties of wide band gap sulfide and oxide semiconducting nanomaterial systems are inherently related to the presence of vacancy-type defects and the experimental techniques of positron annihilation spectroscopy are found very useful in their investigations [1-3]. There are a number of changes that may accompany the nanostructure formation of materials like phase transformation, lattice contraction or expansion, inversion (in spinel materials), free volume generation etc. Positron annihilation parameters are highly sensitive to these changes as the processes involve redistribution of the electrons and hence changes in their annihilation characteristics. In this work, we have tried to establish the utility of these techniques for the studies of a number of aspects of nanostructured semiconductors and highlight the role of vacancy-type defects in the modification of material properties.

2. Experimental details

The samples used in these studies here are prepared through the chemical route, in order to have better control on the temperature of synthesis and also to ensure better purity of the final products. As a general example, we discuss below about the solvothermal process adopted to get nanocrystalline samples of cadmium sulfide (CdS) of grain sizes varying over a wide range even down to 2 nm. A teflon-lined stainless steel chamber of closed cylindrical shape and 110 ml
capacity was used for the purpose. Appropriate amount of CdSO₄ or CdCl₃ or Cd(NO₃)₃.4H₂O and thiourea (NH₂CSNH₂) with molar ratio 1:3 were taken in the chamber and then filled with ethylene glycol (C₂H₆O₂) or benzene up to 80% of its volume. After 30 minutes of stirring, the closed chamber was heated for 12 hours inside a box furnace at the temperature (between 423K and 523K) chosen for the approximate particle size desired to achieve and then cooled down to room temperature. The resulting yellow precipitates were filtered off and washed in ethanol several times to remove the excess traces of reagents. The final products were dried in vacuum at 333K for 6 hrs. The experimental parameters such as the solubility of the Cd sources in the solvent and temperature were varied to get samples of the desired size of CdS nanoparticles. The details of synthesis of the other nanosystems are given in the respective references cited.

The sizes of the nanoparticles were estimated either from x-ray diffraction patterns and/or high resolution transmission electron microscopy images. In carrying out the positron annihilation measurements, a ²²Na source of approximate strength 400 kBq deposited on a thin (~ 2 mg.cm⁻²) Ni foil is kept immersed in the sample (in powder form) taken in a glass tube and the gamma rays were detected using BaF₂-coupled XP2020Q photomultiplier tubes and high pure germanium (HPGe) detectors. The slow-fast gamma-gamma coincidence setup used for positron lifetime measurements had a resolution (FWHM) of 170 ps. The HPGe detectors used for coincidence Doppler broadening (CBD) measurements had energy resolutions 1.27 and 1.33 keV at 511 keV. Typically a million counts were collected under each positron lifetime spectrum and the data were analyzed using the PALSfit program [4]. About 7-8 million coincidence events were generated in each CDB spectrum. The sample and source were maintained under good vacuum conditions to avoid the interference of air and other absorbable gases.

3. Results and discussion
The morphology as well as the sizes of the nanocrystallites play crucial roles in governing the annihilation characteristics of positrons in semiconductors. Positrons can also respond differently to nanosystems of different stoichiometric features. This is evident from figure 1 which shows the peak-normalized positron lifetime spectra for undoped and Mn²⁺-doped zinc sulfide (ZnS) nanorod samples. Figure 2 gives an example where the mean positron lifetime \( \tau_m \) is shown to continuously increase with decrease in diameter of ZnS hexagonal nanocrystals [5].

![Figure 1. Peak-normalized positron lifetime spectra of pure ZnS nanorod sample and after doping with 20% Mn²⁺ ions.](image1)

![Figure 2. The mean positron lifetime versus grain size of ZnS hexagonal nanocrystallites [5].](image2)
An interesting example of positron affinity to open-volume defects is further illustrated in figures 3(a) and 3(b) which show the orthopositronium ‘pick-off’ lifetime $\tau_3$ and its intensity $I_3$ increasing steadily with decreasing grain size in ZnS cubic nanocrystals [5].

Figure 3. (a) Orthopositronium lifetime $\tau_3$ and (b) intensity $I_3$ versus grain size of ZnS cubic nanocrystalline samples [5].

In an experiment conducted to follow the transformation from the hexagonal wurtzite structure to cubic form of nanocrystallites during the substitution by Mn$^{2+}$ ions in ZnS nanorods, as revealed by x-ray diffraction patterns, the positron lifetimes $\tau_1$ and $\tau_2$ and intensity $I_2$ showed distinct features in their variation [6]. The variations of the $S$ and $W$ parameters and, in particular, the $S$ vs. $W$ plot shown in figure 4 also showed the transformation due to the sensitivity of positrons to the accompanying defect evolution processes [6].

Figure 4. $S$-$W$ plot of the Mn-doped ZnS nanorod samples [6].

Figure 5. $S$ parameter versus concentration of Mn doped in ZnS nanocones [9].
A remarkable observation in this study was the collapse of a three-state trapping model situation to a two-state one with the addition of Mn$^{2+}$ ions. The interior of the nanorods became defect-free due to doping [6, 7]. Interestingly, we found no such transformations taking place when identically synthesized ZnS nanoparticles were doped by Mn$^{2+}$ ions [8]. In other words, the morphology of nanosystems has got an important bearing on their structural characteristics.

Positron annihilation studies were also performed on ZnO nanocones doped with Mn$^{2+}$ ions [9]. A significant observation was the continuous decrease of the base diameters of the nanocones from 75 nm to 25 nm when the concentration of Mn$^{2+}$ ions was increased from 0 to 15%. Mn$^{2+}$ ions have a larger radius ($\sim$ 0.80 Å) compared to that of Zn$^{2+}$ (\sim 0.73 Å) and hence the substitution of the latter by the former will result into strain within the nanometer-sized grains. The strain can be gotten rid of by accommodating the Mn$^{2+}$ ions on the surface ionic layer rather than inside the grains. As the concentration of the doped Mn$^{2+}$ ions increase, more surface area is required to contain them and the material takes recourse to the increased surface to volume ratio of smaller nanocones. The $S$ parameter showed a continuous increase due to the annihilation of positrons increasingly at the grain surfaces instead of in the interior of the grains (figure 5).

In another experiment, positron lifetime and Doppler broadening measurements were done on two samples of cadmium oxide (CdO), one composed of pure microoctahedrons and another with nanowires growing out of the octahedron surfaces. Three positron lifetimes were obtained, each representing annihilation through different mechanisms and environments. The longest component $\tau_3$ ($\sim$1.3-1.4 ns) arising from the annihilation of orthopositronium atoms can be ignored, as its intensity $I_3$ ($\sim$0.6%) in both the cases was too small. The other two lifetimes $\tau_1$ and $\tau_2$ were 134 and 323 ps in the case of sample containing only octahedrons and 140 and 342 ps in the other sample. In both the cases, their intensities were the same as 79.1 and 20.3%. As the edge lengths of CdO microoctahedrons were in the range 1.5-3.5 µm, positron annihilations will be taking place within the octahedrons and not on the octahedron surfaces. For the second sample with nanowires on the surfaces also, the octahedrons were of sizes larger than the thermal diffusion lengths for positrons. But a fraction of the positrons got annihilated on the nanowire surfaces, which are rich in defects because of the highly disordered atomic arrangement. Positrons could get trapped into the defects over there and got an enhanced lifetime.

Quantum confinement effects in semiconductor nanomaterials can be studied by positron annihilation techniques with a high degree of success [11, 12]. For example, both the $S$ parameter and the mean positron lifetime $\tau_m$ showed significant increases in the case of cadmium sulfide (CdS) nanocrystalline samples composed of grains whose sizes were below the threshold for observation of the characteristic blue shift in optical absorption studies [11]. Identical observations were obtained in nickel oxide (NiO) nanoparticles synthesized through both solvothermal and sol-gel processes [12]. Positron lifetime $\tau_2$ showed a drastic increase when the grain sizes were below about 7 nm. A more systematic investigation on NiO nanoparticles of different average grain sizes was carried out recently. The optical band gap increased from the bulk value of 3.95 eV to 4.48 eV in nanoparticles of sizes ranging from 15 nm down to 3 nm. The behavior of $\tau_2$ in this case is shown in Figure 6. Detailed analysis is in progress.

The results recently obtained on titanium oxide (TiO$_2$) are partly illustrated figure 7. Details shall be soon published elsewhere. Positron annihilation parameters showed a reversal of variation with annealing temperature due to the transition from the anatase structure to rutile one around 700°C. The shorter lifetime $\tau_1$ in this case was attributed to the bulk lifetime admixed with defects of the mono- and/or divacancy type. The vacancies started annealing above 500°C and the phase transition followed soon after the annealing temperature was raised further high.
A study of doping ZnO with Li$^{3+}$ ions had been conducted recently. Figure 8 shows the variation of $S$ with the doping concentration. The results confirm the interaction of vacancy-type defects present initially in the undoped sample with Li$^{3+}$ ions on doping. The process continues uninterrupted till 16%, the highest doping concentration used in this work. Preliminary results on
Eu-doped CeO nanocrystalline samples are shown in Table 1. The increase in lifetime implies increased positron annihilation on the grain surfaces. Detailed investigations are in progress.

4. Summary and conclusions
In semiconductor nanomaterials, the vacancy type defects need to be precisely characterized not only for the knowledge of their size and concentration, but even for their charge states. Positrons are trapped by neutral as well as negatively charged vacancies or their clusters but get strongly repelled by those with a net positive charge. This is crucial when a measured positron lifetime with larger magnitude needs to be attributed to vacancy clusters. Positronium formation, although of small intensities, cannot be ignored totally as the lifetimes and intensities often exhibit systematic variation with grain size, doping concentration, temperature etc. This calls for precise determination of the defect distribution, their location and even orientation. Some of these issues could be addressed successfully with positron annihilation spectroscopy. Although not discussed in detail in this paper, the CDBS experiments are shown to highlight the differing elemental environments around defects in which positrons get trapped at the different stages of variation of the input parameters. These information can be highly useful in studies involving defect-related properties such as magnetism, heat treatment, cold-work, metallurgy etc.

References

[1] Krause-Rehberg R and Leipner H S 1999 Positron Annihilation in Semiconductors—Defect Studies (Springer-Verlag, Berlin), pp. 1–126.
[2] Kar S, Chaudhuri S and Nambissan P M G 2005 J. Appl. Phys. 97 014301
[3] Brauer G, Anwand W, Grambole D, Grenzer J, Skorupa W, Cizek J, Kuriplach J, Prochazka I, Ling C C, So C K, Schulz D and Klimm D 2009 Phys.Rev. B 79, 115212
[4] Olsen J V, Kirkegaard P, Pedersen N J and Eldrup M 2007 Phys. Stat. Sol. (c) 4 4004
[5] Biswas Subhajit, Kar Soumitra, Chaudhuri Subhadra and Nambissan P M G 2006 J. Chem. Phys. 125 164719
[6] Kar Soumitra, Biswas Subhajit, Chaudhuri Subhadra and Nambissan P M G 2007 Nanotechnology 18 225606
[7] Nambissan P M G, Biswas Subhajit, Kar Soumitra and Chaudhuri Subhadra 2007 Phys. Stat. Sol. (c) 4 3889
[8] Biswas Subhajit, Kar Soumitra, Chaudhuri Subhadra and Nambissan P M G 2008 J. Phys. : Condens. Matter 20 235226
[9] Ghoshal Tandra, Kar Soumitra, Biswas Subhajit, De S K and Nambissan P M G 2009 J. Phys. Chem. C 113 3419
[10] Ghoshal Tandra, Biswas Subhajit, Nambissan P M G, Majumdar Gautam and De S K 2009 Crystal Growth and Design 9 1287
[11] Kar Soumitra, Biswas Subhajit, Chaudhuri Subhadra and Nambissan P M G 2005 Phys. Rev. B 72 075338
[12] Das Soumen, Ghoshal Tandra and Nambissan P M G 2009 Phys. Stat. Solidi C 6 2569

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