The pronounced role of impurity phases in the optical properties of Mn catalyzed ZnS nanostructures

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The pronounced role of impurity phases in the optical properties of Mn catalyzed ZnS nanostructures


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We report the effect of Mn self-doping in Mn catalyzed ZnS nanostructures grown via vapor liquid solid mechanism, which also resulted in the formation of additional impurity minority phases like ZnO and MnO$_2$. The synthesized ZnS nanostructures were subsequently annealed in the range of 500 °C – 700 °C in an inert environment to remove impurity phases and enhance the incorporation of dopant. Room temperature photoluminescence showed strong defect assisted luminescence. It was observed that green emission due to intrinsic defects of ZnS nanostructures was reduced in magnitude and Mn related orange/red luminescence increased in magnitude in nanostructures annealed at high temperature. The presence of impurity phases led to the observation of surface optical and interface phonon modes as observed in the Raman spectroscopy. Dielectric continuum and phonon confinement models were employed to determine the correlation lengths of the optical phonon modes. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4930587]

I. INTRODUCTION

The ongoing research in the nanostructured materials has a potential to make a remarkable change in electronic consumer market due to tailored electronic and optical properties, which have found applications in electronics, spintronics, optoelectronic devices, etc. The unique electronic and optical properties of the low dimensional structures arise due to strong quantum confinement effects. Among these, 1-D nanostructures offer significantly improved properties for applications. The zigzag GaN/Ga$_2$O$_3$ nanowires sensor device has been fabricated for NO gas sensing. Single wall carbon nanotubes have found potential applications in liquid crystal displays, thin film transistors, sensors, optical switches due to excellent electro optical response. Ferrite nanoparticles have been proposed to be helpful in several biomedical applications on targeting, diagnosis and disease treatment.

Several techniques have been employed in the growth of 1-D nanostructures such as electrochemical deposition, solvothermal, homoepitaxial growth, chemical vapor transport, vapor liquid solid, etc. The synthesis of 1D nanostructures by vapor liquid solid (VLS) mechanism is one of the simplest way of growth and is widely used for obtaining single crystalline 1-D nanostructures. The VLS method requires a metal liquid droplet as a catalyst, which adsorbs the gaseous species of the source material followed by the nucleation and growth of the nanowires. The process is thermodynamic driven. It has also been shown that the catalyst droplet can act as a dopant and lead to self-doping in the growing nanostructure. The self-doping of the catalyst during the growth of nanostructures strongly depends on the conditions and can compete with the growth as diffusion of the catalyst atom depends on the growth temperature [e.g., Ref. 14].

ZnS is among the firstly discovered II – VI compound semiconductor materials with a wide band gap of 3.7 eV. It exists in two polymorphic forms; wurtzite and zinc blende, where zinc blende

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is stable at room temperature. Thermal stability and excellent optical transparency are the main reasons for ZnS in the making of optical windows.\textsuperscript{15} ZnS nanostructures have found wide applications in electronics industry, e.g., field emitters, field effect transistors, $p-$type semiconductors, sensors and nanogenerators.\textsuperscript{16} Impurity doping in nanostructures is an effective way to achieve the enhanced optical, electronic and magnetic properties of the host nanostructures.\textsuperscript{17} Metals, such as Mn, Cu, Co, Fe, Ga are chosen as dopants for ZnS nanostructures using various techniques, such as thermal evaporation, sol gel processing, co precipitation, microemulsions, wet chemical methods, etc.\textsuperscript{18} Different visible emission bands have been observed emanating from these dopants, for example, orange luminescence from $^4T_{2g} \leftrightarrow ^6A_{1g}$ transition of Mn in ZnS:Mn doped nanoparticles,\textsuperscript{19} red emission from Eu doped ZnS,\textsuperscript{20,21} green emission attributed to $3d$ transition of Cu in ZnS:Cu doped nanoparticles.\textsuperscript{22,23} The defect states related to Cd\textsuperscript{24} and Fe\textsuperscript{25} have also given rise to green emission in 1-D ZnS nanostructures doped with Cd and Mn/Fe. Among many dopants, Mn has gained much attention due to its efficient light emitting properties from the application point of view.\textsuperscript{18}

However, incorporation of dopant causes structural imperfections in the host lattice symmetry due to number of factors, such as difference in the ionic sizes, oxidation states and electronegativity. It can also alter the concentration of intrinsic defects and thus affect the physical properties. Excess incorporation of Cu in ZnS has been reported to shift the Raman longitudinal optical (LO) phonon modes.\textsuperscript{26} In this case, Cu was incorporated interstitially in the ZnS lattice and induced the tensile stress and structural transformation.\textsuperscript{26} Zhang \textit{et al.}, reported a new line at 338 cm$^{-1}$ identified as the surface optical (SO) phonon mode in ZnS nanowires, which was confirmed by using the dielectric continuum model.\textsuperscript{27} Self-doping of different catalysts (Au, Sn and Mn) in VLS grown ZnS nanostructures have also resulted in a systematic shift in the LO and surface optical (SO) phonon modes. The degree of solubility of the three catalysts in the host structure was determined by the symmetry breaking of the SO mode. The small value of surface corrugation wavelength determined using the dielectric continuum model approximation in the case of Mn and Sn catalyzed ZnS nanowires confirmed the presence of these catalysts near or at the surface of the grown nanostructures.\textsuperscript{14} The dielectric continuum model (DCM) predicts the scalar potentials important in electron phonon interactions.\textsuperscript{28} Dielectric continuum model is described in terms of the dielectric functions of the material and the surface in contact with that material e.g oxide, interface. The dispersion of SO phonons depends upon dielectric constants of the surrounding media. The interface phonon modes originate at the interface formed by different dielectric function surfaces and it travels along the interface.\textsuperscript{29}

For the interpretation of Raman spectra, several models have been employed extensively, which included microscopic force model,\textsuperscript{30} bond polarization model,\textsuperscript{31,32} and spatial correlation model.\textsuperscript{33} Fauchet and Campbell generalized the spatial correlation model, originally proposed by Ritcher for the interpretation of Raman lineshape observed from the microstructures. The proposed model included the breaking of selection rules that allowed first order scattering at the first Brillouin Zone (BZ), which resulted in the change of lineshape and peak positions.\textsuperscript{34,35}

In this paper, the effect of annealing in inert atmosphere on two different morphologies of Mn self-doped ZnS nanostructures (namely, nanowires and nanobelts) under identical conditions is reported using room temperature photoluminescence and Raman spectroscopies. Mn doped 1-D ZnS nanostructures were synthesized using vapor liquid solid (VLS) technique. The morphology and structure of the synthesized nanostructures were determined from the scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies, respectively. The as grown structures were annealed at 500°C, 600°C and 700°C in a flowing Ar environment. Optical characterization included room temperature photoluminescence spectroscopy (PL) and Raman spectroscopy of the as-grown and annealed nanostructures. The effect of geometry of the two nanostructures on the photoluminescence and Raman modes was probed. Correlation lengths of the LO and SO phonon modes were determined by spatial correlation model by fitting the experimental curves of the two geometries.

\section*{II. EXPERIMENT}

Mn as catalyst (1 nm thin layer) was deposited on $n$–Si (100) substrates with a native oxide layer (2 – 3 nm) in UHV chamber at a base pressure of $\sim 10^{-7}$ torr. ZnS nanostructures were grown by placing the ZnS powder (0.5 g, 99.99\% pure) in an alumina boat at the center of the horizontal
tube furnace. Mn coated Si substrates were kept at 850 °C and 675 °C. ZnS powder was heated to 1020 °C and the vapor flux was transported from the boat to the Mn coated Si substrates by the carrier gas (95% N$_2$ + 5% H$_2$) at a flow rate of 60 Sccm. The growth was carried out for 2 hours. The synthesized nanostructures were annealed at three different temperatures, i.e., at 500 °C, 600 °C and 700 °C in Ar flowing at 200 Sccm for 2h and were characterized for each annealed temperature.

Morphology, structure and phase identification were done by SEM (SU-1500 Hitachi) and XRD (Panalytical XpertPro), respectively, of the as – grown and annealed ZnS nanostructures. The PL spectra were collected at room temperature by exciting at 325 nm with a He-Cd laser. The Raman spectra were collected with Horiba Jobin Yvon (T-6400 Raman spectrometer), and LabRaman by Dongwoo Optron with an excitation energy of 514 nm. All spectra were corrected for the detector response.

III. RESULTS AND DISCUSSION

A. Structural analysis

The Figure 1(a) – 1(f) shows the scanning electron microscopy images (a, b) and the X-ray diffraction patterns (c,d) of the as grown and (e,f) annealed at 700 °C ZnS nanostructures, respectively. The average radius of nanowires was 0.9 ± 0.2 µm and the average dimensions of the synthesized nanobelts were 0.5 ± 0.1 µm (thickness) and 5.0 ± 2.0 µm (width), respectively, as determined from the SEM images. It was noticed that the surface area of nanobelts (850 µm$^2$) was almost three times greater than (225 µm$^2$) nanowires. This has a significant effect on the optical properties of these nanostructures as was observed in the Raman spectroscopy.

From the X-ray diffraction patterns of the as grown and annealed ZnS nanostructures as shown in Figure 1(c), 1(d) and 1(e), 1(f), respectively, the diffraction peaks were identified as reflections from (100), (002), (110) planes of the ZnS wurtzite phase. The reflection peaks observed at different values of 2θ in the scanned range were identified by matching with the standard reference cards of possible products, i.e., ZnS (00-036-1450), ZnO (00-0664), ZnO$_2$ (00-013-0311), MnS (01-1089), MnO (04-0326), MnO$_2$ (01-0799) and elemental Mn (00-001-1234) and (00-001-1237). Interesting to note was the presence of impurity phases in the as grown and annealed nanostructures like MnS/MnS$_2$, MnO$_2$ and ZnO/ZnO$_2$.

Presence of oxides confirmed the impure growth environment. Another possible source of oxygen would have been the disassociation of oxygen from the native SiO$_2$ layer. With annealing, Mn was expected to dope uniformly in the host lattice. In addition, another impure phase MnS$_2$ appeared in the XRD patterns, which was the result of loss of Zn and O in nanostructures. The formation of impurity phases and incorporation of Mn in ZnS nanostructures resulted in shift of diffraction peaks. The shift in the “d” spacing of various reflection planes were used to determine the average residual strain in the host lattice by using ($\varepsilon = \frac{d_1-d_o}{d_o}$), where $d_1$ was the d spacing in the as grown and 700 °C annealed nanostructures and $d_o$ was the d spacing for each reflection place taken from the reference card (JCPDS 00-036-1450).

The average value of strain in the host lattice increased from 4.87 x 10$^{-3}$ (3.14 x 10$^{-3}$) in the as grown to 6.02 x 10$^{-3}$ (5.59 x 10$^{-3}$) in the annealed (700 °C) nanowires (nanobelts). It was observed that the change in the residual strain in nanowires was small compared to nanobelts. This was quite evident from the XRD patterns of annealed nanostructures (Figure 1(e), 1(f)), where significant reflections from impurity phases were observed in the case of nanobelts. The possible cause for this difference was due to different growth temperatures, which led to different stoichiometric ratio of ZnS and Mn in both kinds of nanostructures.

B. Photoluminescence

Room temperature photoluminescence spectra collected in the visible region from the as grown and annealed ZnS nanowires and nanobelts are shown in Figure 2(a) and 2(b), respectively. The observation of broad asymmetric band meant the presence of number of contributions in it. Asymmetric broad emission band centered at around 550 nm was observed in both nanostructures, which
was resolved by fitting with multi-Gaussian functions as shown in the bottom two spectra of Figure 2. Out of three, one of the resolved PL band in the range 550-560 nm (yellow) was due to Zn vacancies in the ZnS nanowires. The other resolved PL band in the range 600 – 620 nm (orange/red) was due to the doped Mn in the host lattice and was attributed to the transitions between $^4T_1$ to $^6A_1$ state of Mn$^{2+}$ doped inside the ZnS nanowires with tetrahedral coordination. The green emission observed in the range 520 – 540 nm (green) was assumed to have originated from the ZnO and its origin was attributed to oxygen vacancies. A weak tail extending to 700 nm was also observed and attributed to originate from MnO$_2$ in the as grown ZnS nanowires.

The contribution of each component, i.e., the integrated intensity, was determined from the fits of the PL spectra of the as grown and annealed ZnS nanostructures. There was reduction in the green emission and an increase in the orange/red emission from the as grown nanostructures to 500 °C – 700 °C annealed nanostructures. The strong variation in emission bands was due to variation in the intrinsic as well as extrinsic defects as mentioned above. As observed in the XRD analysis, the doping of Mn improved and became uniform with annealing temperatures in annealed ZnS nanostructures. Mn in ZnS lattice can be incorporated either at an interstitial site or replacing...
Fig. 2. Room temperature photoluminescence spectra of the as grown and annealed (at 500°C, 600°C and 700°C) ZnS nanostructures; (a) nanowires, and (b) nanobelts. Bottom spectra in both columns show the fits.

Zn site in the lattice. The location of Mn strongly affected the existence of Zn and S vacancies. Mn, if incorporated minutely into the ZnS lattice could activate or deactivate Zn related vacancy defects by replacing Zn in the ZnS lattice to affect the green emission. This was the case observed in the annealed nanostructures. Annealing of nanostructures at high temperature resulted in uniform distribution of Mn in ZnS and reduction in the Zn vacancies, which resulted in quenching of the green emission. It also increased Mn luminescent centers for orange/red emission,\textsuperscript{38} and this led to the increased orange/red emission in the annealed nanostructures.

It was observed from the PL spectra that oxygen vacancies increased in ZnS nanowires (nanobelts) with annealing from 4\% (2\%) to 13\% (10\%) from 500°C to 700°C, respectively. This was due to strong reduction in the MnO\textsubscript{2} phase from 32\% in the as grown to 11\% in 700°C annealed ZnS nanobelts. Thus, the PL results thus confirmed the findings of the XRD.

C. Raman spectroscopy

The study of Raman modes by means of Raman spectroscopy is an excellent tool to determine the structural deformation or imperfections. Figure 3(a) and 3(b) shows the LO and SO Raman modes appeared as doublet obtained in the as grown and annealed ZnS nanowires and nanobelts, respectively. The two insets show the complete Raman spectra of the as grown nanowires (Figure 3(a) inset) and nanobelts (Figure 3(b) inset). Sharp peaks observed at 351 cm\textsuperscript{-1} and 274 cm\textsuperscript{-1} corresponded to Raman A\textsubscript{1}/E\textsubscript{1} LO mode and A\textsubscript{1}/E\textsubscript{1} TO modes, respectively. Peaks observed at 219 cm\textsuperscript{-1} and 366 cm\textsuperscript{-1} were due to combination of acoustic overtones and were assigned to (TO – TA) and (TO + TA) Raman modes.\textsuperscript{39} The peak observed at 158 cm\textsuperscript{-1} was assigned to the second order disorder activated (DA) mode and most probably was present due to the doping of the catalyst.\textsuperscript{40,41} The SO mode appeared as a broad asymmetric feature centered at 341 cm\textsuperscript{-1} and was interestingly resolved by precisely fitting three Gaussian functions centered at 340 cm\textsuperscript{-1}, 341 cm\textsuperscript{-1} and 342 cm\textsuperscript{-1}. The SO mode is expected to be very sensitive to the existence of impurity modes at the surface and the formation of interfaces. This was concluded from the dielectric continuum model as given in the following section. In a pure ZnS nanostructure with lateral surface symmetry breaking, a single symmetrical peak at 340 cm\textsuperscript{-1} is expected due to surface optic phonon mode of the ZnS. However, the presence of asymmetry
FIG. 3. SO and LO phonon modes of the as grown and annealed (a) nanowires, and (b) nanobelts. The insets (i, ii) show the complete Raman spectra of the two nanostructures, and (iii) shows the fitting of the SO phonon mode with multi Gaussian functions.

in the SO mode meant the presence of additional modes in the vicinity of the SO mode. Thus the SO mode observed was believed to have contributions from the SO phonon mode of ZnS, MnO$_2$ phase and interface phonon mode at 342 cm$^{-1}$, 341 cm$^{-1}$ and 340 cm$^{-1}$, respectively. The interface phonon mode had possibly originated from the existence of ZnS/ZnO interfaces. DCM model was employed to determine the contribution of each mode and fit the SO lineshape. In the calculations, it was assumed that very thin discontinuous layers of ZnO and MnO$_2$ were present at the surface of nanowires. The XRD and PL results have already confirmed that the synthesized ZnS nanostructures had impurity ZnO and MnO$_2$ phases.

The mixed optical phonon modes present in nanostructures were calculated considering double layered structures (ZnO/ZnS or MnO/ZnS) as shown in the inset of Figure 4. The range of frequencies for the optical phonon modes in wurtzite nanowires is given by Ref. 43 and is plotted in

FIG. 4. Plot of $\gamma$ as a function of $\omega$. The inset represents the cross-sectional schematic along the length axis displaying non-uniformly dispersed ZnO and MnO$_2$ segments in the ZnS matrix, used in the calculations.
Figure 4:

\[ \gamma = \text{sign} \left( \frac{\varepsilon_{zi}(w)}{\varepsilon_{ti}(w)} \right) \left( \frac{\varepsilon_{zi}(w)}{\varepsilon_{ti}(w)} \right)^{\frac{1}{2}} \]

where \( \varepsilon_{ti}(= \varepsilon_{0}^{r}e^{2}w_{L}^{2}T_{i}^{-1}) \) and \( \varepsilon_{zi}(= \varepsilon_{0}^{r}e^{2}w_{L}^{2}T_{i}^{-1}) \) are the tangential and normal permittivity of the host medium. Generally, there exist five distinct types of optical phonon modes in bi-layered wurtzite nanowire systems. The first is the interface optical (IO) phonon mode, which correspond to the decaying waves on both sides of the interface with \( \varepsilon_{zi} \varepsilon_{ti} > 0 \) \((i=1,2)\). Second is the quasi-confined mode, which are oscillating waves with \( \varepsilon_{zi} \varepsilon_{ti} < 0 \) and decaying with \( \varepsilon_{zi} \varepsilon_{ti} > 0 \). Third is the half space like mode with decaying one having \( \varepsilon_{zi} \varepsilon_{ti} > 0 \), and oscillating with \( \varepsilon_{zi} \varepsilon_{ti} < 0 \). Fourth is the propagating mode with \( \varepsilon_{zi} \varepsilon_{ti} < 0 \) \((i=1,2)\). Fifth is exactly the confined mode with frequency \( \omega_{c1} \).

It can be seen in Figure 4 that interface phonon modes for wurtzite ZnS/\( ZnO \) interfaces and hence the contribution of the IO phonon mode of the ZnS nanowires. This was consistent with the PL results, in which oxygen vacancies increased in the decrease in \( ZnO \) phase and also increased the eect of symmetry breaking at the surface to

The solution of the Laplace Equation in cylindrical coordinates is given as:

\[ \phi(\rho) = e^{im\theta}e^{ikz} \times \begin{cases} A_{1}I_{m}(k\rho) & \rho \leq R_{1} \\ A_{2}I_{m}(k\rho) + B_{2}K_{m}(k\rho) & R_{1} < \rho < R_{2} \\ \end{cases} \]

where \( \rho = R_{1} + R_{2} \) and \( R_{1} = 0.66 \mu m, R_{2} = 0.22 \mu m \) (average values as determined from SEM).

Applying boundary conditions and solving Laplace Equation to determine the ratio of \( \frac{\varepsilon_{1}}{\varepsilon_{2}} \)

For nanowires \( \frac{\varepsilon_{1}}{\varepsilon_{2}} = \frac{L_{m+1}(k\rho)}{I_{m+1}(k\rho)} \left[ \frac{K_{m+1}(k\rho) + B_{2}/A_{2}K_{m+1}(k\rho)}{I_{m+1}(k\rho) + B_{2}/A_{2}K_{m+1}(k\rho)} \right] \)

For nanobelts \( \frac{\varepsilon_{1}}{\varepsilon_{2}} = tanh kx \)

Where \( \varepsilon_{1} = \varepsilon_{\infty 1} + \frac{\varepsilon_{\infty 1} - \varepsilon_{\infty 2}}{1 - \frac{\varepsilon_{\infty 1}}{\varepsilon_{\infty 2}}} \) and \( \varepsilon_{2} = \varepsilon_{\infty 2} + \frac{\varepsilon_{\infty 2} - \varepsilon_{\infty 1}}{1 - \frac{\varepsilon_{\infty 2}}{\varepsilon_{\infty 1}}} \). The value of \( \omega_{c1} \) for ZnS/\( ZnO \) interface is 340 cm\(^{-1}\) and 410 cm\(^{-1}\), which exactly matched the experimentally observed values.

The contribution of each component was also determined from the fits of SO mode. The contribution of 340 cm\(^{-1}\) peak decreased from 40% in the as grown samples to 30% in 700 °C annealed ZnS nanowires. This was consistent with the PL results, in which oxygen vacancies increased in the annealed nanowires and the extent of ZnO and MnO phases were reduced. This confirmed the reduction of ZnO/ZnS interfaces and hence the contribution of the IO phonon mode of the ZnS/ZnO interface also decreased. On the other hand, contribution of the SO phonon mode of the ZnS increased from 28% in the as grown to 70% in the 700 °C annealed ZnS nanowires. Thus, the appreciable increase in oxygen vacancies in nanostructures annealed from 500 °C to 700 °C resulted in the decrease in ZnO phase and also increased the effect of symmetry breaking at the surface to
increase the contribution of SO phonons. The shift in the Raman modes was the result of induced strain in annealed nanostructures as observed in Figure 3. The shift in Raman modes is related to strain as can be seen in the following relation:\(^4\)

\[
\frac{\Delta \omega}{\omega_0} = \left(1 + \frac{3\Delta c}{c}\right)^\gamma + 1
\]

(6)

Where \(\gamma = 0.95\) for ZnS.

It was determined that the change in strain increased from 0.1\% to 0.3\% (0.01\% to 0.014\%) for the case of nanobelts (nanowires). This observation was also in accordance with the XRD findings, which showed that strain increased from 0.3\% (as grown) to 0.6\% (annealed) in nanobelts was large compared to increase in strain in nanowires from 0.5\% (as grown) to 0.6\% (annealed) in nanowires. This was attributed to the role of difference in geometries of nanostructures. This was further explored by studying the correlation lengths of LO and SO phonon modes in two kinds of nanostructures.

1. **Correlation lengths of LO and SO Raman modes**

The full width half maximum (FWHM) of the LO and SO modes was used to determine the correlation lengths of the two optical modes of the nanostructures. Phonon confinement model (PCM) was applied to determine the correlation length of the LO phonon modes.\(^4\) Raman intensity lineshape \(I(\omega)\), is given by Eq. (6) using Gaussian confinement function for Wurtzite phases.

\[
I(\omega) \approx \int \frac{dq}{\omega - \omega(q)} + (T/2)^2
\]

(7)

where

\[
|C(q,0)|^2 \approx e^{-q_1^2L_1^2/16\sigma^2} e^{-q_2^2L_2^2/16\sigma^2} \left[1 - \text{erf}\left(\frac{iqL_2}{\sqrt{32\pi}}\right)\right]^2
\]

(8)

Where \(\omega(q)\) is the phonon dispersion, \(\Gamma\) is natural linewidth and \(C(q,0)\) is the Fourier coefficient of the phonon confinement function. For the Wurtzite phase, \(L_1\) is the correlation length and \(L_2\) is the length of the structures. The fits of the SO and LO phonon modes as observed in the nanowires and nanobelts is shown in the Figure 5(a) and 5(b), respectively, which gave the correlation lengths in the as grown and annealed nanowires and nanobelts, respectively. The correlation length of the SO mode for nanobelts was small, which was due to enhanced inhomogeneity and impurities on the surface of nanobelts.

**FIG. 5.** Experimental (black lines) and calculated (open red circles) SO and LO modes lineshapes of the as grown and annealed ZnS (a) nanowires, and (b) nanobelts. The fitting was used to determine the correlation length in two types of nanostructures.
The SO mode lies between the LO and TO Raman modes and Lyddane Sachs Teller relation \( \omega_{TO}^2 = \omega_{LO}^2 \epsilon_\infty / \epsilon_0 \) was used to determine the TO frequency (\( \omega_{TO} \)); where \( \epsilon_\infty = 8.29 \), \( \epsilon_0 = 5.11 \) for ZnS. The symmetric and anti-symmetric curves of the SO phonon mode were calculated from Eq. (9) and Eq. (10) using dielectric continuum model.

\[
\omega_{SO}^2(q)_{S} = \frac{\epsilon_\infty \tanh(qL_2/2) + \epsilon_m}{\epsilon_\infty \tanh(qL_2/2) + \epsilon_m} \omega_{TO}^2
\]

\[
\omega_{SO}^2(q)_{AS} = \frac{\epsilon_\infty \coth(qL_2/2) + \epsilon_m}{\epsilon_\infty \coth(qL_2/2) + \epsilon_m} \omega_{TO}^2
\]

Figure 6 shows the dispersion curves of the symmetric and anti-symmetric SO phonon modes of the as grown and annealed nanostructures as a function of \( qL/2 \). The \( q \) values of the as grown and annealed nanostructures were found by considering average length of 40 nm for nanowires and 35 nm for nanobelts. The variation in the correlation lengths is shown in Figure 7. Interestingly, the correlation lengths were more or less similar in the two geometries. The correlation length of the SO mode was higher than the LO mode, which suggested the quality of surface was better compared to the bulk. The correlation length of the LO phonon mode decreased from 15 nm to 9 nm in the as grown to the annealed (700 °C) nanostructures. This also indicated that Mn was present in the bulk and its incorporation in the host lattice improved with annealing. A linear decrease in the LO correlation length of nanostructures with annealing temperature was due to better incorporation of Mn in the host lattice. The increase in the correlation length of SO in the ZnS nanostructures annealed at 700 °C was due to appreciable formation of MnS\(_2\) phase. The initial decrease in the correlation length of SO phonon modes in the annealed nanostructures were due to migration of defects from the bulk to the surface. The increase in the correlation length in the ZnS nanostructures annealed at 700 °C was due to possible removal of interfaces formed by ZnS with oxides. Thus annealing at 700 °C or higher is not advisable as it led to formation of additional impurity (MnS\(_2\)) phase.

![Figure 6](image-url)
IV. CONCLUSION

In conclusion, ZnS nanostructures contaminated with impurity phases and defects were studied for their role in the structural and optical properties. Annealing improved the quality of synthesized nanostructures as oxygen related defects were reduced considerably. A new phase of MnS₂ appeared in nanostructures annealed at high temperature. X-ray diffraction results showed a high value of stress in nanowires compared to nanobelts, which was attributed to smaller volume of nanowires. Photoluminescence spectroscopy of the two nanostructures showed identical results and confirmed the role of impurity phases and defects. A strong SO Raman mode was observed in the vicinity of the LO Raman mode, which showed the symmetry breaking at the surface of nanostructures. The correlation lengths of the two modes were determined from the lineshape analysis using dielectric continuum and phonon confinement models. A variation in the correlation lengths showed the Raman modes were sensitive to the presence of impurity phases and defects.

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