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Effects of doping on the surface energies of nanocrystals and evidence from studies at high pressure

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1. Introduction

Nanometer-scale semiconductor crystallites have been extensively studied in order to explore their unique properties and potential applications [1,2]. Much effort has been focused on II-VI semiconductor nanocrystals [3-7], where doping is fundamental to controlling the properties [8]. The doped ions are mainly distributed on the surfaces of the nanocrystals [9]. So an interesting question is that of what surface-related properties would be brought about by the doped ions on the surface. The surface and interfacial energies are the most important physical attributes of nanomaterials because the ratio of surface to volume will increase with crystal size decreasing. The surface and interface energies greatly affect the physical properties of nanomaterials. An anomalous behavior of nanomaterials as regards the surface energy often induces many novel nanosize effects, which open up many possibilities for technological applications [10]. However, so far the research on nanomaterial surface energy has been mainly restricted to theoretical studies. It is essential to develop new experimental tools and methods for understanding nanomaterial surface energy. Here, we investigate the effects of doping on the surface energies of nanocrystals and use high pressure methods to prove the change in surface energy.

ABSTRACT

 $Zn_{1-X}Mn_XS$ (X = 0.85% and 1.26%) nanoparticles have been synthesized using a specially designed equipment and we have studied the influence of doping Mn^{2+} on the surface energy of ZnS. The high pressure behaviors of ZnS nanocrystals with different dopant contents have been investigated using angle-dispersive synchrotron X-ray powder diffraction up to 45.1 GPa. Theoretical calculations show that doping with Mn^{2+} increases the surface energy of the nanocrystals. The theoretical result has been further corroborated by our experimental observation of an increase in the phase transition pressure of Mn^{2+} doped ZnS nanocrystals in diamond-anvil-cell studies.

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2. The experiment

Dilute magnetic semiconductor $Zn_{1-x}Mn_xS$ nanoparticles were synthesized through the reaction between the solution and H₂S at the gas-liquid interface, using new equipment, as seen in Fig. 1(a). H₂S gas was generated by dropping HCl into a Na₂S aqueous solution. The method enabled avoidance of the side effects caused by other impurities [11]. The synthesis procedure can be described as follows. The solution was prepared from the analytical reagent Zn(CH₃COO)₂·2H₂O and Millipore water. The ion concentration of Zn^{2+} in the solution was 2 \times 10⁻³M and the ion concentration of Mn^{2+} in the solution was adjusted by using $Mn(CH_3COO)_2 \cdot 4H_2O$. The concentration of the surfactant hexadecyl trimethyl and ammonium bromide in the solution was 9×10^{-5} M. The mixed solution was first heated to 75 °C using microwaves, and then it was dripped and spread out on the wetted convex surface. Nitrogen carried the H₂S gas into the growth chamber and this reacted with the cations on the thin gas-liquid interface. The synthesized nanoparticles were then collected into the receiving chamber, filled with disodium ethylene diamine in tetraacetate solution. The reaction process could be controlled by adjusting the concentration of H₂S gas and the dripping rate of the solution. The nanoparticles were rinsed with Millipore water and with ethanol at least three times.

For high pressure experiments, the synthesis sample was loaded into a hole of 90 μ m diameter in a compressible gasket of stainless steel. Small ruby chips were placed into the sample chamber for pressure measurements using the



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Fig. 1. (a) A schematic diagram showing the central configuration of the synthesis system for $Zn_{1-x}Mn_xS$ nanoparticles. (b) The representative morphology of $Zn_{1-x}Mn_xS$ nanoparticles. (c) The X-ray powder diffraction patterns for three synthesized samples corresponding to solutions containing different Mn^{2+} ion concentrations. (d) The high resolution TEM image of the $Zn_{1-x}Mn_xS$ nanoparticles. The inset gives the electron diffraction powder pattern of the sample.

quasihydrostatic ruby pressure scale. The pressure-transmitting medium was a methanol–ethanol (4:1) mixture. We confirmed that quasihydrostatic conditions were maintained throughout the experiments. The precision of our pressure measurements was estimated to be around 0.05 GPa. The high pressure X-ray diffraction patterns and spectra were measured *in situ* up to 43.5 and 45.1 GPa, respectively, for nanocrystals with different Mn²⁺ doping levels by using an angle-dispersive X-ray diffraction source ($\lambda = 0.386556$ Å) at beam line X17B3 of the National Synchrotron Light Source at Brookhaven. The Bragg diffraction rings were recorded with an imaging plate detector.

3. Results and discussion

The morphology of the nanoparticles was characterized by using transmission electron microscopy (TEM). The nanoparticles were assembled according to size, with diameters of about 50-150 nm, as seen in Fig. 1(b). Three synthesized samples corresponding to solutions with different Mn²⁺ ion concentrations were characterized by using X-ray powder diffraction, as seen in Fig. 1(c). The result shows that the structures of the samples were the same. The three peaks correspond to the (111), (220), and (311) planes of the zinc-blende (ZB) structure. The broadened diffraction peaks were caused by the small sizes of the nanocrystals. The nanocrystal size was estimated at about 4 nm using the Debye-Scherrer formula. By the refinement of the X-ray powder diffraction with different Mn^{2+} doping contents, the peaks for (220), (111) and (311) all shift toward the small angle direction. Among these shifts, there was a relatively major shift toward the small angle direction in the (311) lattice planes when the Mn²⁺ ions in the solutions reached a 30% mole fraction. This could be due to the fact that the radius of the ${\rm Mn}^{2+}$ ion is larger than that of ${\rm Zn}^{2+}$ and caused the crystal lattice to expand. The doped contents of the three samples were analyzed by using energy-dispersive Xray spectroscopy. The result shows that the mole percentages of



Fig. 2. (a) ZB structure model with surface atoms. (b) ZB structure model with one surface Zn atom replaced by one Mn atom in a (311) lattice plane.

the doped contents for the samples were 0.85% and 1.26%, which correspond to mole percentages of 2% and 30% $\rm Mn^{2+}$ ion content solutions respectively.

To understand how the doped ions influence the surface energy of the nanocrystals, we calculated the total energies of the doped and undoped structures, and compared the total energies between the two. The calculations were performed by means of the pseudopotential plane wave density of the functional method implemented in the CASTEP code treatment within the Materials Studio package.

The X-ray powder diffraction results for different Mn^{2+} doping content nanocrystals indicated that the locations of the Mn^{2+} were mainly in (311) lattice planes. We established two ZB structure models with surface atoms; one was the pure ZB structure, and the other had one Mn atom replacing a Zn atom in the (311) lattice plane, as seen in Fig. 2.



Fig. 3. X-ray diffraction patterns collected at various pressures for different Mn^{2+} doped ZnS samples. The peaks derived from the gasket are distinguished from reflections of $Zn_{1-x}Mn_xS$ by using "G" markings. (a) X-ray diffraction patterns for the sample doped with 0.85% mole per cent of Mn^{2+} content. The right inset shows X-ray diffraction patterns collected at 17.7 GPa pressures for the sample doped with 0.85% mole per cent of Mn^{2+} content. (b) X-ray diffraction patterns for the sample doped with 1.26% mole per cent of Mn^{2+} content. The right inset shows X-ray diffraction patterns collected at 18.3 GPa pressures for the sample doped with 1.26% mole per cent of Mn^{2+} content.

The calculated results show that total energy of undoped ZB structure is -23398.755 eV and the total energy of the doped ZB structure with one Mn atom replacing a Zn atom in the (311) lattice plane is -22317.960 eV. The energy difference between the two structures comes from the doping of the Mn^{2+} ion on the surface. The doping of Mn^{2+} leads to an increase of the total energy which is just the increase in the surface energy.

Fig. 3 shows in situ XRD experiments on Mn²⁺ doped ZnS samples in a diamond anvil cell (DAC) at room temperature at pressures up to 43.5 and 45.1 GPa. The diffraction patterns of samples at ambient pressure can be indexed to a cubic structure with space group F43m(NO.216). With increase of the pressure, the diffraction lines shift toward higher angles and the ZB peak intensity weakens. For samples doped with 0.85% mole per cent of Mn^{2+} content, a new peak starts to emerge at approximately 17.7 GPa, as shown in the Fig. 3(a) inset on the right, suggesting that a transition had occurred at this pressure. According to the indexing result, this indicates that the new diffraction peak corresponds to the (200) line of rock-salt structure. We consider this new structure to be the rock-salt (RS) phase [12]. With the pressure increasing to 18.9 GPa, the RS (111), (220), (400) and (420) peaks begin to appear, and the ZB (220) and (311) peaks start to fade, indicating a small pressure range where the RS and ZB phases coexist. At 21.9 GPa, the ZB (111) peak also disappears and the RS (200) peak intensity becomes quite pronounced, suggesting that the phase transition is finished. For the sample doped with 1.26% mole per cent of Mn²⁺ content, the phase transition occurs at 18.3 GPa, as shown in the Fig. 3(b) inset on the right, and finishes at 22.2 GPa. With the doping content increasing, the phase transition pressures of the nanocrystals also increase.

For some nanocrystals, the size dependence of the solid–solid phase transition is attributed to the increase of the surface energy [13–15]. Nanocrystals having higher surface energies would cause the increases in phase transition pressures which we observed experimentally, because a higher pressure is required to overcome the extra surface energy. Previous results reported by some research groups showed that the transition pressure for bulk ZnS is more than 13 GPa, and that for the 4 nm ZnS nanocrystals is 16 GPa [16]. In our studies, the phase transition pressure for 4 nm doped ZnS nanocrystal is even higher. Our result shows that doping with Mn^{2+} leads to higher surface energy, and thus, higher phase transition pressure can

be used as an important tool for probing the surface energies of nanocrystals.

4. Conclusions

In conclusion, we have synthesized $Zn_{1-x}Mn_xS$ nanoparticles using new equipment and studied the influence of doped Mn^{2+} on the ZnS surface energy. Theoretical calculations show that the doping with Mn^{2+} increases the surface energy of the nanocrystals. The theoretical result was further corroborated by our experimental observation of an increase in the phase transition pressure of Mn^{2+} doped ZnS nanocrystals in diamond-anvil-cell studies.

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