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BRIEF REPORTS

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review B** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Size-induced transition-temperature reduction in nanoparticles of ZnS

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X-ray-diffraction studies of nanometer-sized particles of zinc sulfide show a significant reduction in the zinc-blende-to-wurtzite phase transition temperature, as compared to the bulk value. Five nanoparticle samples were annealed in vacuum at temperatures increasing from room temperature (23 °C) to 500 °C. Post-anneal analyses revealed an increase of crystallite size, accompanied by a partial transformation from the cubic, zinc-blende structure to the hexagonal, wurtzite structure at temperatures as low as 400 °C. This is significantly less than accepted bulk transition temperature of 1020 °C. The particles also show some lattice distortion with decreasing particle size and there is a monotonic reduction in the specific volume of about 2.3% as the particle size decreases from about 240 to about 30 Å. [S0163-1829(99)04837-7]

ZnS is an important material for a variety of applications such as electrolumiscent devices, solar cells, and other optoelectronic devices. Nanometer-sized semiconductor particles have attracted much attention because of their novel electronic and optical properties originating from quantum confinement.[1] Recently, nanometer-sized particles of PbS, CdS, and CdSe showed distortion from the lattice of bulk materials and the presence of strain with reduced particle size.[2–4] Although a variety of polytypes were observed for bulk ZnS by x-ray investigations, they are all related to two basic structures: the cubic zinc-blende structure (3C) and the hexagonal wurtzite structure (2H).[5] The most stable form of zinc sulfide is the cubic structure and in the bulk it transforms to wurtzite structure at 1020 °C. The bulk zinc sulfide melts at a temperature of 1650 °C. Recently Goldstein *et al.* reported that nanoparticles of CdS melt at a substantially reduced temperature.[6]

In this paper, we report structural studies of nanoparticles of zinc sulfide at various annealing temperatures under vacuum conditions. The starting particle size of zinc sulfide was 2.8 nm. These particles were synthesized using a technique in which the bicontinuous cubic phase exhibited by some lipids and surfactants is used as a matrix to provide a uniform nanometer-sized reaction chamber for the formation of nanoparticles.[7] High-resolution transmission electron microscopic (TEM) studies showed that the particles are highly monodispersed (std. dev.$<7\%$). High-resolution TEM images show that the particles are monocrystalline and indicate a small anisotropy in shape.

X-ray-diffraction scans were taken on a Rigaku diffractometer using Cu $K\alpha$ radiation from a rotating anode x-ray generator operating at 50 kV and 200 mA. The as-made nanocrystalline ZnS sample was divided into four portions for annealing in vacuum at four different temperatures. A zirconium oxide crucible with a diameter of 1.25 cm and height of 1.9 cm was filled with the sample and placed into a resistive heater made of Pt foil, mounted on a removable vacuum flange. A Pt-Pt (10% Rh) thermocouple was inserted into the middle of the powder sample to measure the temperature. In several hours, the sample chamber was initially pumped down to a vacuum of 3×10^{-7} Torr using a 6-inch liquid-nitrogen-trapped oil diffusion pump. The sample was then heated at a rate of 20°/m, until the final desired temperature was reached. During the heating, considerable outgassing was observed. For short times, the pressure in the vacuum chamber was as high as 1×10^{-5} Torr, but within a few minutes after reaching the final temperature, the pressure would stabilize to the high 10^{-7} Torr region. After 45 min of annealing at the desired temperature, the sample was cooled to room temperature at a rate of about 15–20°/min. This procedure was carried out for four samples separately annealed at four temperatures, $300°\pm2°$, $350°\pm2°$, $400°$

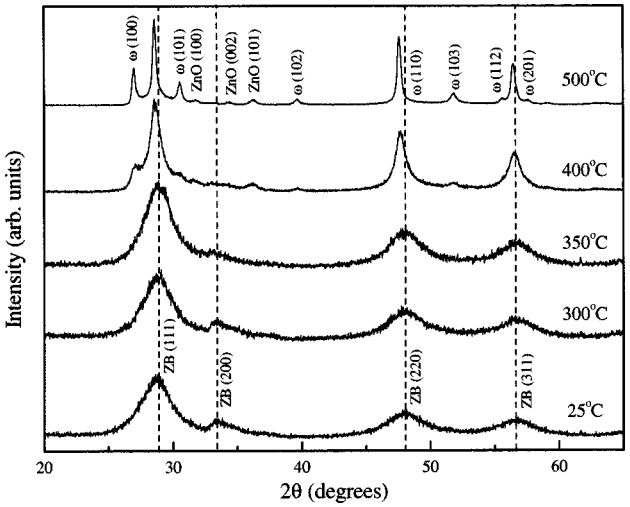

FIG. 1. $\theta/2\theta$ scans of ZnS samples annealed at various temperatures taken with Cu $K\alpha$ radiation. Peaks labeled with zb and w correspond to the zinc-blende and wurtzite structures, respectively.

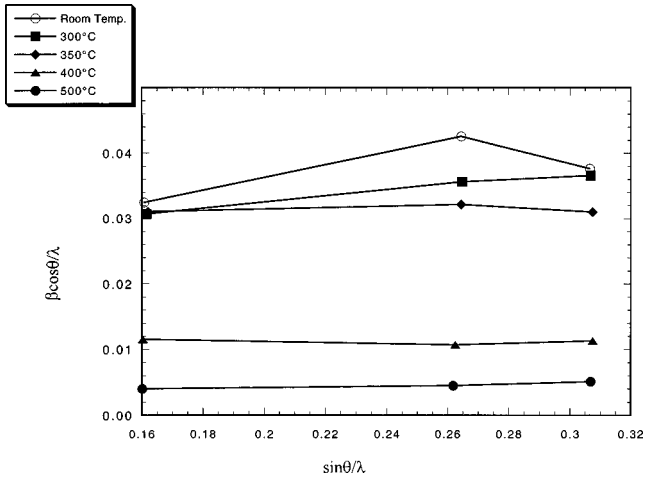

FIG. 2. $\beta\cos\theta/\lambda$ versus $\sin\theta/\lambda$ for the five samples whose $\theta/2\theta$ scans are shown in Fig. 1. Different symbols correspond to different annealing temperatures as shown in the inset.

$\pm 2°$, and $500° \pm 5$ °C. After annealing at the specified temperatures, the samples were mounted on silicon wafer for diffraction scans.

Figure 1 shows the $\theta/2\theta$ diffraction scans for each of the four annealed samples and the starting material. Below 350 °C, the ZnS nanoparticles showed only the zinc-blende phase. The lattice parameters were calculated using a least-squares refinement. The unit cell below 350 °C showed distortion from cubic symmetry and the best fit was obtained using a tetragonal unit cell. The results of the calculation of the unit-cell parameters, particle size, and unit-cell volumes are given in Table I. The unit-cell volume was reduced by nearly 2% when compared with the unit-cell volume of the bulk ZnS (bulk lattice parameter $= 5.405$ Å). The samples annealed at above 350 °C showed mixed phases of the zinc-blende and wurtzite structures. The peaks labeled in Fig. 1 with the *w* symbol refer to the *hkl* indices of the wurtzite structure. For both the phases of the 400 and 500 °C annealed samples, the lattice parameters conformed with the bulk values of ZnS. The volume fraction of each phase was estimated based on the integrated intensities of the diffraction peaks of the wurtzite (002) and zinc-blende (111) peaks. In addition to the presence of the two phases of the ZnS, peaks corresponding to zinc oxide (zincite) are also present. The volume fraction of ZnO is estimated to be less than 4%, based on the measured intensities of the ZnO-diffraction peaks. The information on the strain and the particle size was obtained from the full widths at half maximum (FWHM) of the diffraction peaks. After applying the correction for instrumental broadening, the FWHM's can be expressed as a linear combination of the contributions from the strain and particle size through the following equation:

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\eta\sin\theta}{\lambda},$$

where β is the measured FWHM in radians, θ is the Bragg angle of the diffraction peak, λ is the x-ray wavelength, ε is the effective particle size, and η is the effective strain. A plot of $\beta\cos\theta/\lambda$ versus $\sin\theta/\lambda$ for the five samples is shown in Fig. 2. Essentially all the samples show the absence of any significant strain. Only the room-temperature sample shows

TABLE I. Calculated values of the unit-cell parameters, specific volumes, and particle sizes.

Annealing temperature	Phase	Percent of phase	Lattice parameters (Å)	Specific volume (Å^3)	Particle size (Å)
23 °C	Zinc-blende	100	$a = 5.42 \pm 0.01$ $c = 5.28 \pm 0.02$	38.8 ± 0.3	27
300 °C	Zinc-blende	100	$a = 5.42 \pm 0.01$ $c = 5.27 \pm 0.01$	38.7 ± 0.2	29
350 °C	Zinc-blende	100	$a = 5.41 \pm 0.01$ $c = 5.29 \pm 0.02$	38.7 ± 0.3	32
400 °C	Zinc-blende	72	$a = 5.404 \pm 0.012$	39.5 ± 0.3	74
400 °C	Wurtzite	28	$a = 3.82$ $c = 6.26$	39.5	74
500 °C	Zinc-blende	72	$a = 5.41$	39.6	232
500 °C	Wurtzite	28	$a = 3.82$ $c = 6.26$	39.6	243

that there may be some nonuniform strain and departure from uniform shape along the different crystallographic orientations.

The data suggest that for the nanometer-sized particles of ZnS, the equilibrium transition temperature for the cubic-to-wurtzite transition is significantly reduced from the bulk value. As the particles undergo transformation, there is a tendency for the particles to merge thereby increasing the average particle size. In a solid-solid phase transition, there are two exchange energies involved, that liberated because the free energy of the new phase is less than that of the old phase, and the surface energy required to form the interface between the two phases. The boundary energy must be provided, whereas the excess free energy is liberated. Therefore, it is energetically favorable to reduce the total surface area and this will happen if the particle size were increased. This result is consistent with the observations of Goldstein *et al.*[6] who observe the melting temperature of nanoparticles of CdS to be substantially reduced over the bulk value.

It also is likely that, if the samples were held at the annealing temperatures for a longer period of time, a greater portion would have undergone the transition. We cannot claim that equilibrium was achieved at any of the anneal temperatures.

We also notice from the data in Table I that there is about a 2.3% increase in the specific volume as the particle size increases from about 30 to about 240 Å. This could be explained by the fact that as the particle sizes increase, the effect of the surface forces on the bulk become progressively less.

To assess the size and morphology of the particles before and after annealing, we performed transmission electron microscopy (TEM; 200 kV). Figure 3 shows TEM micrographs of the ZnS nanoparticles after annealing at 500 °C. Initially the particle size is approximately equal to the crystallite size, indicating that the particles are monocrystalline. No change was observed in the particles after annealing at 300 and 350 °C. After annealing at 400 °C, the particle sizes ranged from 8 to 20 nm and many of the particles are faceted. The onset of the zinc-blende to wurtzite transition is accompanied by a change in the particle size and morphology. Finally, after annealing to 500 °C, most of the particles are faceted and the particle sizes range from 20 to 50 nm. Since the volume of each particle is larger than the crystalline domains, the particles probably are polycrystalline.

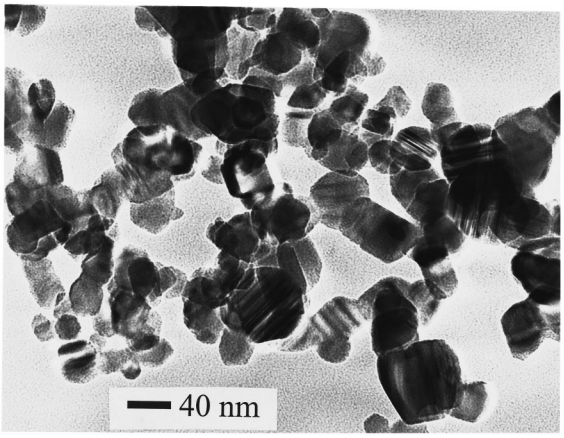

FIG. 3. TEM micrograph of ZnS nanoparticles after annealing at 500 °C.

In conclusion, in the nanometer-sized ZnS particles, the equilibrium transition temperature from the zinc-blende to wurtzite structure is significantly reduced as compared to the bulk value. The nanometer-sized particles show distortion from the cubic lattice of ZnS.

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