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Grain-size effect on pressure-induced semiconductor-to-metal transition in ZnS

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The grain-size effect on the semiconductor-to-metal transition in ZnS has been investigated by *in situ* high-pressure electrical resistance and optical measurements. It is found that the grain-size effect can elevate the transition pressure of ZnS in a larger pressure range. On the basis of the results obtained and results reported in the literature, we demonstrate that the dangers of using the transition pressures of the II–VI compounds as pressure calibrators without a detailed knowledge of their grain-size effects on the transition pressures cannot be overstressed. © *1999 American Institute of Physics.* [S0021-8979(99)03922-5]

The semiconductor-to-metal transitions in a few II–VI semiconductor compounds are used to establish the fixed-point static pressure calibration curve in the pressure range from 15 to 25 GPa for the multianvil high-pressure apparatus, which has been used in many disciplines, e.g., geoscience, materials science, and physics.[1] Among them is the ZnS semiconductor, which has been investigated for many decades.[2,3] Substantial discrepancy in the magnitude of the transformation pressure for ZnS reported in literature has been suggested due to three possible reasons: (1) the different techniques used to identify the transition; (2) various nonhydrostatic conditions in the different pressure apparates; and (3) different systematic errors of the pressure calibration at different groups. Here we report another factor, the grain size of crystals, which can influence the semiconductor-to-metal transition pressure. We clearly show evidence that a reduction of the grain size can substantially elevate the transition pressure of ZnS.

Three ZnS samples with average grain sizes of approximately 10 μm, 36, and 11 nm, were investigated. ZnS powder (10 μm) with a 99.9% purity was used as a starting material for the synthesis of nanometer-sized ZnS samples using a Planetary ball mill (Fritsch Pulverisette 5), with tungsten carbide vials and balls. A single phase with a sphalerite structure (B3) in the samples studied was confirmed by x-ray powder diffraction. The average grain sizes of milled samples and the starting material were estimated by x-ray powder diffraction and by scanning electron microscopy, respectively. High resolution transmission electron microscopy measurements revealed the presence of lattice fringes and confirmed the B3 structure in the samples. Tungsten con-

tamination in the milled samples, originating from the abrasion of the vial and balls, was found to be less than 0.5 at. % from the energy dispersive x-ray analysis.

High-pressure *in situ* electrical resistance measurements at ambient temperature were carried out at Bayreuth, Germany in a 1200 ton multianvil apparatus using 10 and 7 mm edge length octahedral pressure cells. Copper foils were used as electrodes to measure the dc resistance across a sample disk of approximate dimensions 0.9 mm diameter and 0.5 mm thick. Resistance measurements were made on increasing pressure using a previously determined pressure calibration that is based on several pressure standards, including ZnS. However, in this study, we are interested in the relative change in pressure, at which the semiconductor-to-metal
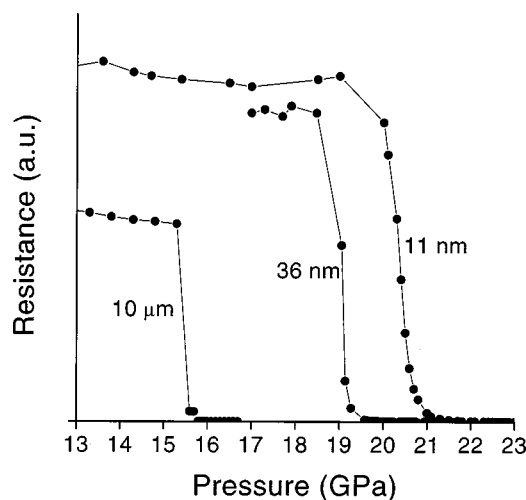

FIG. 1. High-pressure *in situ* electrical resistances for ZnS materials with average grain sizes of 10 μm, 36, and 11 nm at ambient temperature.

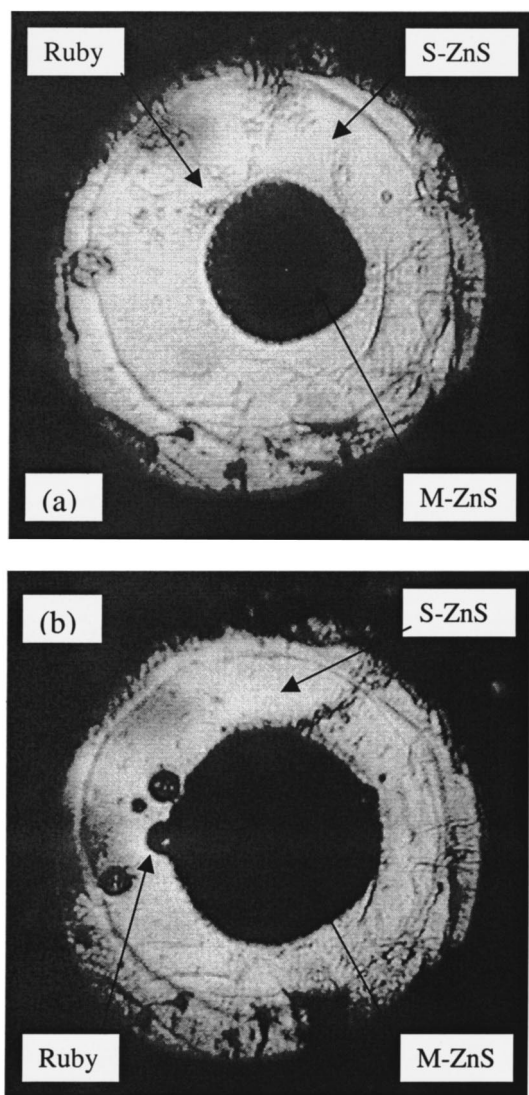[a)]Author to whom correspondence should be addressed; electronic mail: jiang@fysik.dtu.dk

FIG. 2. High-pressure *in situ* optical micrographs of the semiconductor-to-metal transitions for ZnS materials with average grain sizes of 10 μm (a) and 11 nm (b). The transition pressures were determined to be 21.8 ± 0.6 and 16.0 ± 0.5 GPa for 11 nm and 10 μm ZnS samples, respectively.

transition is observed for samples with different grain sizes.

High-pressure *in situ* optical measurements for ZnS materials with average grain sizes of 10 μm and 11 nm were performed in a Mao-Bell type diamond anvil cell with 0.4 mm flat culet in Paris, France. The powder samples were directly compressed in a 0.4 mm hole of a nickel gasket without pressure transmitting medium. The pressure was measured by using small ruby chips placed on the top diamond. The high-pressure metallic phase (M–ZnS) is opaque compared with the low-pressure semiconducting phase (S–ZnS), so that the phase boundary is quite well defined. By increasing the applied load to the diamonds the limit of the high-pressure phase moves in the pressure gradient and the transition pressure was accurately measured when the phase boundary was just crossing a ruby chip.

Figure 1 shows high-pressure *in situ* electrical resistances for ZnS materials with average grain sizes of 10 μm, 36, and 11 nm. It is clearly seen that the semiconductor-to-

metal transition occurs at pressures of approximately 19.0 ±0.4 and 20.5 ± 0.6 GPa for the 36 and 11 nm ZnS, respectively, whereas for the 10 μm ZnS it occurs at approximately 15.6 ± 0.3 GPa. We further performed high-pressure optical measurements for the 11 nm ZnS as well as the 10 μm sample for comparison, as shown in Fig. 2. It is found that the semiconductor-to-metal transition for the 11 nm ZnS [Fig. 2(b)] appears at around 21.8 ± 0.6 GPa while the 10 μm sample [Fig. 2(a)] has a transition at around 16.0 ± 0.5 GPa, in good agreement with the data obtained in Fig. 1. Our experimental data reveal that the semiconductor-to-metal transition pressure strongly depends on the grain size of ZnS crystals. The smaller the crystal, the higher the transition pressure.

Recently, the issue of the effects of crystallite size on structural stability in nanocrystals has been shown to be of considerable interest from a fundamental viewpoint, and also with respect to the applicability of these materials. Over the last few years x-ray powder diffraction using synchrotron radiation has been intensively applied to study the effects of crystallite size on structural stability in nanocrystals. Tolbert *et al.*[4–6] reported their studies on Si, CdSe, and CdS nanocrystals and found that the smaller the crystallite, the higher the transformation pressure. They explained the increase in transition pressure for the nanocrystals in terms of surface-energy differences between the phases involved. An enhancement of transition pressure in nanocrystals ZnO compared with corresponding bulk material was also observed.[7] Qadri *et al.*[8] have also reported that the effect of reduced particle size in PbS nanocrystals is to elevate the transition pressure while the compressibility increases with decreasing particle size. However, Jiang *et al.*[9] reported that for nanometer-sized γ-Fe$_2$O$_3$ particles the phase transition pressure (from γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$) is lower than for bulk material. A similar result was also reported in TiO$_2$ for the rutile-to-α-PbO$_2$ transition.[10] The authors suggested the larger volume change upon transition in the nanocrystals than in bulk being the main factor. It seems that the grain-size effect on the structural stability can be of either sign with respect to the change of the transition pressure, depending on the system under investigation.

On the basis of the results obtained for the ZnS samples and results reported in the literature, therefore, it can be concluded that the dangers of using the transition pressures of the II–VI semiconductor compounds as pressure calibrators without a detailed knowledge of their grain-size effects on the transition pressures cannot be overstressed.

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