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2008 J. Phys.: Condens. Matter 20 345224

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Non-monotonic size dependence of the elastic modulus of nanocrystalline ZnO embedded in a nanocrystalline silver matrix

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Received 11 June 2008, in final form 15 July 2008

Published 6 August 2008

Online at stacks.iop.org/JPhysCM/20/345224

Abstract

We present the first high pressure Raman study of nanocrystalline ZnO with different average crystallite sizes. The problem of low Raman signals from nanometer-sized particles was overcome by forming a nanocomposite of Ag and ZnO nanoparticles. The presence of the nanodispersed Ag particles leads to a substantial surface enhancement of the Raman signal from ZnO. We find that the elastic modulus of nanocrystalline ZnO shows a non-monotonic dependence on the crystallite size and suggest that the non-monotonicity arises from an interplay between the elastic properties of the individual grains and the intergranular region.

A decrease in the crystallite size is usually found to produce an increase in the bulk modulus [1, 2] though certain exceptions are known [3]. The observed elevation of the bulk modulus with decreasing size has so far been rationalized on the basis of the surface energy of the nanoparticles being greater than that of the bulk [4]. There are several reports of the measurement and calculation of the elastic modulus of isolated ZnO nanowires [5, 6] and nanobelts [7], and the elastic modulus is generally found to increase significantly with decreasing wire diameter. However, we do not know of any study of the size dependence of the elastic properties of nanocrystalline ZnO. In this paper, we present a study of the effect of crystallite size on the elastic modulus of nanocrystalline ZnO thin films, obtained from high pressure Raman spectroscopy. The nanocrystalline ZnO thin films studied by us are essentially random mosaics of crystallites (see figure 1(a)). We show that the elastic modulus of such a system is a non-monotonic function of the crystallite size, and attribute this behavior to a competition between the elastic properties of individual nanodomains and those of the inter-crystalline region. The application of stress on a system results in the development of strain, to which phonon frequencies are extremely sensitive. Variable pressure Raman spectroscopy is therefore a very powerful technique for studying elastic properties, but often suffers from extremely

low signal intensities, especially for nanocrystalline samples. We succeeded in circumventing this difficulty by using a dilute, random dispersion of nanocrystalline Ag in a ZnO matrix (also nanocrystalline), which leads to substantially intensified signals due to the surface enhancement mechanism [8].

Magnetron sputtering at relatively high ambient pressure and low substrate temperature is known to produce nanocrystalline thin films in which the grain size can be controlled by proper choice of process parameters [9]. A ZnO target (50 mm diameter, 3 mm thick) was prepared by pressing ZnO powder (99.99%) at 0.3 GPa and annealing at 400 °C in Ar. Two small silver pieces were placed on the horizontally mounted ZnO target. Nanocomposite films of Ag and ZnO (nc-ZnO/Ag) with different average particle sizes were deposited on glass substrates (at 300 K) by sputtering from the ZnO/Ag composite target. RF sputtering was carried out typically at 100–150 W power under 5–200 mTorr Ar pressure. The as-prepared films, with a black metallic luster, were peeled off the glass substrate and used for further studies. Transmission electron microscope (TEM) observations indicate that the Ag nanoparticles formed a dilute dispersion in the nanocrystalline ZnO matrix. The darker regions in figure 1(b) are the Ag nanoparticles while the ZnO nanoparticles exhibit a lighter contrast. The coherently diffracting crystallite size (ξ) was estimated from an analysis of the x-ray diffraction line broadening. The line profile analysis, performed using the GSAS software [10], provided the full

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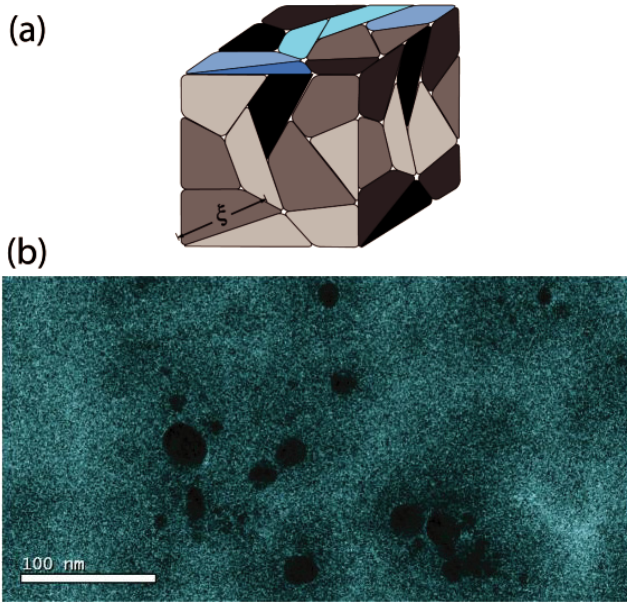


Figure 1. (a) Schematic representation of the random mosaic structure of nanocrystalline domains with an average crystallite size ξ . (b) Transmission electron micrograph of the Ag nanoparticles (darker contrast) dispersed in the nanocrystalline ZnO matrix. (This figure is in colour only in the electronic version)

width at half-maximum (FWHM), β , for a number of diffraction peaks. The crystallite sizes were then obtained from the FWHM using the Williamson–Hall method [11]. The refined x-ray diffraction patterns and the corresponding Williamson–Hall plots for a few representative samples are shown in figure 2.

Raman scattering measurements were performed in the backscattering geometry using a Jobin Yvon T64000 Raman

spectrometer equipped with an inverted microscope. The excitation source was the 514.5 nm line of an Ar⁺ laser operated at a power of about 100 mW, measured at the sample. Figure 3(a) shows the Raman spectrum of bulk ZnO powder. The spectrum shows the A₁(TO) mode at 381 cm⁻¹, the E₁(TO) at 412 cm⁻¹, the E_{2h} at 438 cm⁻¹ and the E₁(LO) mode at 580 cm⁻¹. The comparatively broad feature at 537 cm⁻¹ has been attributed to a combinational mode (CM) [12]. Figure 3(b) shows the Raman spectrum of the nc-ZnO/Ag nanocomposite at ambient pressure. The CM and the E₁(LO) modes for the ZnO phase in the nc-ZnO/Ag sample are redshifted to 484 cm⁻¹ and 560 cm⁻¹, respectively. The observed redshift of the Raman modes in nc-ZnO/Ag can be attributed to finite size effects that lead to a breakdown of the wavevector selection rule and allow phonons away from the Brillouin zone center to also participate in the Raman scattering process. In addition, the tensile stress at the ZnO/Ag interface, arising from a difference in their thermal expansion coefficients, may also contribute to the redshift. A key feature of the Raman spectra of nc-ZnO/Ag is the absence of the normally strongest E_{2h} mode. This may be explained by the fact that the LO mode gets selectively enhanced under resonant conditions due to the breakdown of the wavevector-dependent scattering rules arising from the contributions to the scattering intensity from the three-band electro-optic Raman tensor [13]. This suggests that the presence of nanodispersed Ag in the nanocrystalline ZnO matrix generates a resonance-like condition [13].

High pressure experiments were performed in a gasketed Mao–Bell type diamond anvil cell (DAC) with a 4:1 mixture of methanol and ethanol as the pressure transmitting medium. A stainless steel gasket was pre-indented to 80 μm and a 200 μm hole was mechanically drilled at the center. Before and after recording each Raman spectrum, the pressure was measured using the fluorescence emission of a small ruby piece

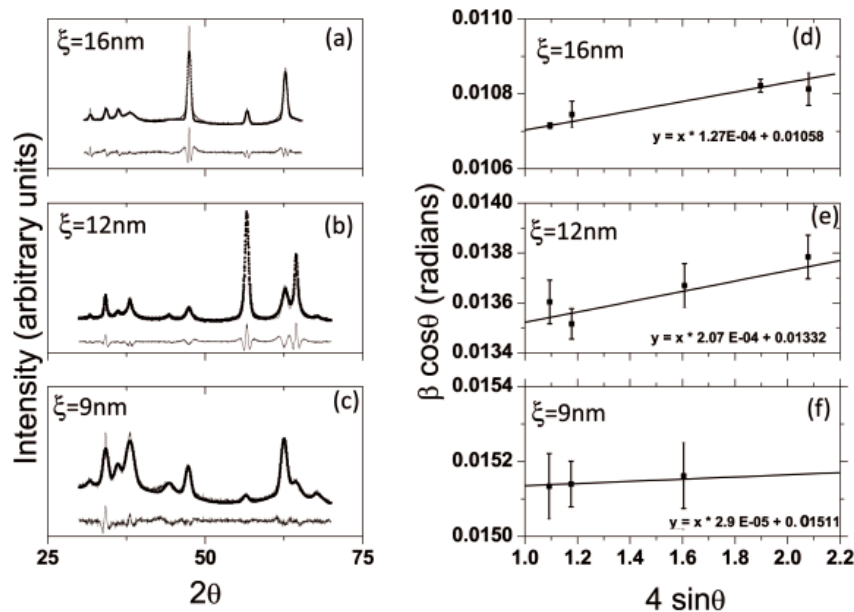


Figure 2. X-ray diffraction profile fits ((a), (b) and (c)) using GSAS and the corresponding Williamson–Hall plots ((d), (e) and (f)) for samples with ZnO particle sizes: $\xi = 16, 12$ and 9 nm, respectively. The solid lines show linear fits to the Williamson–Hall plots of $\beta \cos \theta$ versus $\sin \theta$.

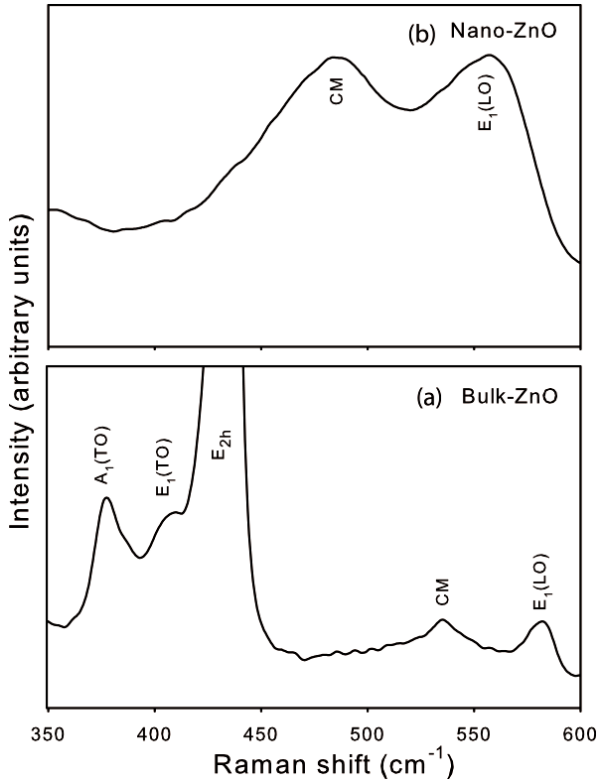


Figure 3. Room temperature and ambient pressure Raman spectra of (a) bulk ZnO powder and (b) nanocomposite ZnO/Ag samples with an average particle size of 16 nm. The Raman mode assignments are shown in the figure.

placed close to the sample in the gasket. In these experiments, the maximum pressure applied was 10 GPa. We have restricted our experiments to below 10 GPa to avoid the known experimental issues regarding the non-hydrostatic nature of the pressure transmitting medium [14]. Figure 4 shows the pressure dependence of the Raman modes with increasing and decreasing pressure for representative nc-ZnO/Ag samples with crystallite sizes (for the ZnO phase) of 16, 12 and 9 nm. Both the $E_1(\text{LO})$ and the CM modes were found to increase monotonically with pressure.

Bulk ZnO is known to undergo a crystallographic phase transition from the wurtzite to the cubic structure at 9–10 GPa [15, 16]. Since there are no Raman-active phonons in the cubic phase, the wurtzite to cubic transition is necessarily associated with a dramatic decrease in the Raman intensity [15]. However, we observed no such transition in nanocrystalline ZnO thin films up to 10 GPa. It is interesting to point out that a size-induced elevation of the structural transition pressure has been observed earlier [17]. Figure 5 shows the variation of the mode frequency of the $E_1(\text{LO})$ Raman mode as a function of increasing and decreasing pressure for three different nc-ZnO/Ag samples with mean sizes: 9, 12 and 16 nm. Clearly, the $E_1(\text{LO})$ mode frequency increases linearly with pressure for all crystallite sizes. The shift in the mode frequency is proportional to the strain, while the applied pressure is equivalent to the stress. The value of $(\Delta\omega/\Delta p)$ for the $E_1(\text{LO})$ mode was calculated from the

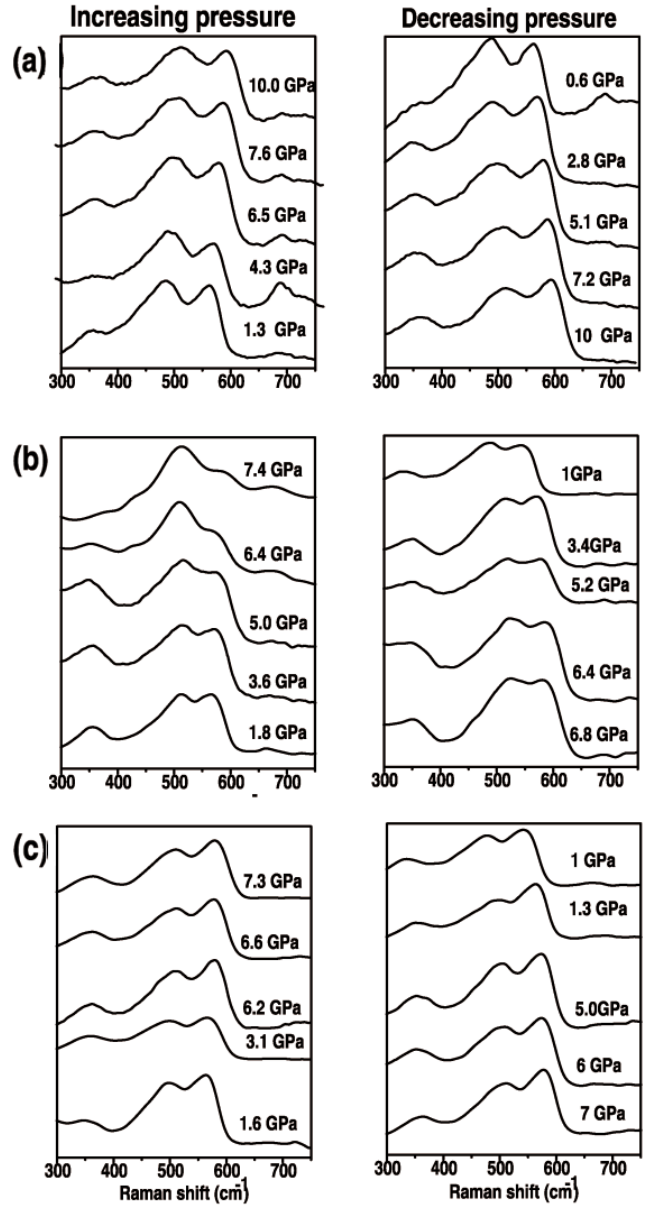


Figure 4. The Raman spectra of nc-ZnO/Ag samples recorded at different pressures. The left panel shows data recorded while increasing pressure while the right panel shows decreasing pressure data for samples with average particle size of: (a) $\xi = 16$ nm, (b) $\xi = 12$ nm and (c) $\xi = 9$ nm.

Raman data for each nanocomposite system to obtain the average elastic modulus, defined as $G = \text{stress/strain} = (\Delta\omega/\Delta p)^{-1}$.

In the present experiment the pressure transmitting liquid would usually not reach the surface of each ZnO nanocrystal. Such a non-hydrostatic pressure condition would generally allow volume-conserving as well as shape-conserving deformations. The elastic energy per unit volume (U) associated with a general deformation (u) is given by [18] $U = \mu(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}^2) + \frac{1}{2}K u_{ll}^2$, where K is the bulk modulus and μ is the shear modulus. The bulk modulus is associated only with a hydrostatic compression which results in a change in volume but not in shape. Since the pressure conditions are

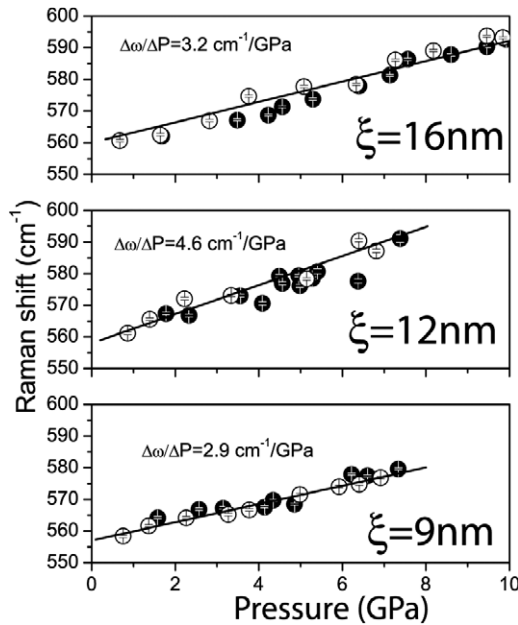


Figure 5. Variation of the E_1 (LO) Raman mode with pressure for nc-ZnO/Ag samples with average particle sizes of 16, 12 and 9 nm. The respective crystallite sizes (ξ) and values of $\Delta\omega/\Delta p$ are indicated in the figure. The closed circles represent increasing pressure runs while the open circles represent decreasing pressure runs.

not hydrostatic in the present experiments, a direct extraction of parameters such as the bulk modulus (K) from high pressure Raman experiments is technically not possible. We therefore study the variation of $(\Delta\omega/\Delta p)^{-1}$, which is a measure of an *average elastic modulus* as a function of the crystallite size (ξ). Interestingly, figure 6 shows that the average elastic modulus, $(\Delta\omega/\Delta p)^{-1}$, is *not* a monotonic function ξ , exhibiting a well-defined minimum at about 13 nm.

To understand the observed elastic behavior of nc-ZnO/Ag, we model each nanocrystalline grain of size ξ in terms of a crystalline core of elastic modulus E_C , and an intergranular region of average thickness L and elastic modulus E_I . The elastic modulus of the nanocomposite system is thus $G = (1 - p)E_C + pE_I$, where $p \propto L/\xi$ is the volume fraction of the intergranular region. All the individual nanocrystalline domains are assumed to have the same crystal structure, varying only in the crystallographic orientation. Since the atomic structure in the intergranular region is generally believed to be disordered and amorphous-like, we can assume that $E_C > E_I$ [19]. With a decrease in size, the volume fraction occupied by the intergranular region is expected to increase, which would result in the overall reduction of G . However the increase in G observed at still smaller sizes probably indicates an increase in the value of E_C , which could arise from a build up of the residual compressive stress in the bulk [20].

In summary, we have reported the first high pressure Raman study of nanocrystalline ZnO for a range of crystallite sizes from 9 to 16 nm. We have circumvented the problem of low Raman signals from nanoparticles by incorporating nanocrystalline Ag with nanocrystalline ZnO in the form of

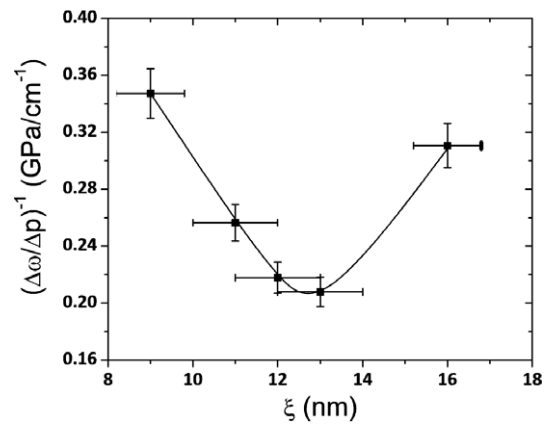


Figure 6. Variation of $(\Delta\omega/\Delta p)^{-1}$ with size (ξ) for the ZnO nanocrystals. ξ was obtained from x-ray diffraction line profile analysis using the Williamson–Hall method.

a random dispersion. The presence of the nanodispersed Ag particles leads to a surface enhancement of the Raman signal from the host (nano-ZnO). Finally, we have shown that the average elastic modulus of nanocrystalline ZnO shows a non-monotonic variation with crystallite size. We suggest that the non-monotonic behavior is due to an interplay between the elastic properties of the individual grains and those of the intergranular region.

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