**Size-dependent photoelastic effect in ZnO nanorods**


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Manipulation of internal strain by an external light beam called photoelastic effect has been firmly established in ZnO nanorods. The underlying mechanism of this interesting phenomenon arises from the combination of the screening of internal electric field and converse piezoelectric effect. We demonstrate that the photoelastic effect is more pronounced in thinner nanorods due to a larger surface to volume ratio. In addition to giving a good evidence for the existence of photoelastic effect in semiconductor nanorods, our finding also provides an excellent possibility for the development of nanoscale optical modulators.

ZnO has been extensively studied due to its unique optical properties in the ultraviolet (UV) region as well as a large exciton binding energy of 60 meV, which holds the promise for producing efficient room temperature exciton emitters and very low-threshold lasers. Recently, quasi-one-dimensional nanoscale ZnO attracted a considerable amount of research interest as a prime candidate for nanoscale optoelectronics applications, including photodetectors, light emitting diodes, and lasers. Additionally, due to a large surface to volume ratio of the inherent nature of nanostructures, ZnO nanorods have been found to exhibit several intriguing phenomena, such as high sensitivity and fast response for the detection of gas molecules and an interesting behavior called photoelastic effect. The photoelastic effect is defined as an external electromagnetic wave capable of producing a change in the internal strain of a material. It is known that ZnO is a good piezoelectric material, in which an electric field can induce a strain and vice versa. Because oxygen defects have been well established to exist on the surface of ZnO, they have the ability to trap electrons, thereby creating a surface electric field. This process results in an upward band bending near the surface. Through the converse piezoelectric effect, ZnO nanorods will embody an internal stress. After photon excitation, the spatially separated photoexcited carriers can screen the built-in electric field and change the internal strain. Therefore, an incident light beam is able to induce a change in the internal strain, which leads to the so-called photoelastic effect. In this paper, we further explore the characteristic of this interesting property by studying its size dependence in ZnO nanorods. It is found that with decreasing diameter of ZnO nanorods, the magnitude of photoelastic effect increases. As a consequence, one can manipulate the photoelastic properties of ZnO nanorods via their diameters, a trait that is very useful for the application of optoelectric devices based on ZnO nanorods.

ZnO nanorods were grown on a-plane sapphire substrates via the vapor-liquid-solid (VLS) growth process as described in our previous report. To manipulate the diameter of ZnO nanorods, we coated Au film with different thicknesses onto different areas of a piece of sapphire substrate. After VLS growth process, ZnO nanorods with a larger diameter will be grown on the area with a thick Au film. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM 6500 system. Microphotoluminescence (micro-PL) and micro-Raman scattering measurements were all performed at room temperature in a backscattering geometry using a Jobin-Yvon T64000 system. The sample was excited by a continuous wave He–Cd laser working at 325 nm, and a neutral density filter was used to control the laser intensity.

As shown in Fig. 1, three different sizes of ZnO nanorods have been grown. The ZnO nanorods form a well-organized hexagonal shape with diameters of [Fig. 1(a)] 300–350, [Fig. 1(b)] 150–250, and [Fig. 1(c)] 70–100 nm. In order to test the influence of size on the optical properties of ZnO nanorods, we performed micro-PL measurements as shown in Fig. 2. The sharp UV emission can be attributed to the band-edge transition, while the broad visible emission is due to the surface-defect-state transition. It is worth noting that with increasing diameter of ZnO nanorods, the surface-defect emission decreases, while the band-edge emission enhances. The variation in intensities of band-edge emission and surface-defect emission can be attributed to the difference in the surface to volume ratio of nanorods with different diameters. More specifically, the relative intensity between the band-edge and surface-defect emissions can be described by

![FIG. 1. SEM images of ZnO nanorods with different diameters of (a) 300–350, (b) 150–250, and (c) 70–100 nm.](http://apl.aip.org/apl/journal/fig?DOI=10.1063/1.3072350)
our experimental data can be well interpreted in terms of determined by experiments. As shown in the inset of Fig. 2, where $C$ and $t$ are constants, which could be determined by experiments. As shown in the inset of Fig. 2, our experimental data can be well interpreted in terms of Eq. (1).

$$I_{BE} = C \left( \frac{r^2}{2rt - r^2} - 1 \right),$$

where $I_{BE}$ and $I_{SD}$ are the PL intensities of band-edge emission and surface-defect emission, respectively, $r$ is the radius of nanorods, while $C$ and $t$ are constants, which could be determined by experiments. As shown in the inset of Fig. 2.

As shown in Figs. 3(a) and 4(a), we can clearly see that the peak position of the band-edge emission of ZnO nanorods shows a blueshift with increasing excitation power density, while the $A_1$(LO) phonon energy shows a low-frequency shift in Raman scattering spectra. Note that the heating effect due to light illumination was not significant in our measurements because it would otherwise result in a reduction in the PL peak energy. This phenomenon can be explained based on the underlying mechanism of the photoelastic effect as follows. Under optical excitation, the photoexcited electrons and holes are swept in opposite directions by the built-in electric fields. The electrons accumulate at the center of the nanorods, while the holes get confined at the surface and neutralize the negatively charged states. Upon further increasing excitation power, more photoexcited holes can significantly neutralize the negatively charged states. The enhanced screening effect will decrease the built-in electric field and diminish the band bending near the surface, therefore, the transition energy gets higher as shown in Figs. 3(b) and 3(c). Besides, the screening of the built-in electric field by photoexcited electron-hole pairs will reduce the internal strain through the piezoelectric effect. Therefore, the stressed ZnO lattice tends to be relaxed and the $A_1$(LO) phonon energy in the Raman spectra is redshifted as shown in Fig. 4(a).

Since the photoelastic effect comes from the existence of defect states on the surface of ZnO nanorods, a larger photoelastic effect in thinner nanorods could be expected due to their larger surface to volume ratio. This prediction has been examined by the measurement of excitation-power-dependent micro-PL on ZnO nanorods with different diameters as shown in Fig. 3(a). It is clear that the peak position of band-edge emission shifts toward the high-energy side with increasing excitation power, and the amount of blueshift in thinner rods is much more than that in thicker rods. This result confirms the inherent nature of the photoelastic effect that ZnO nanorods with a smaller diameter have a larger...
surface to volume ratio and will exhibit a larger photoelastic effect.

We also examined the dependence of the $I_{BE}/I_{SD}$ ratio on the excitation power as shown in Fig. 3(d). It displays that the $I_{BE}/I_{SD}$ ratio increases with increasing pumping power density. According to the underlying mechanism of the photoelastic effect, this phenomenon can be understood as follows. Under a higher excitation power, a larger amount of electron-hole pairs are generated, which provides a higher probability to screen the built-in electric field. As a result, the formation of excitons become much easier and the band-edge emission is enhanced. Besides, due to the reduction in the built-in electric field, the photoexcited holes become harder to be driven to the surface, and the emission arising from surface defects is therefore quenched. This result thus gives additional evidence supporting our interpretation of the photoelastic effect in ZnO nanorods.

To further confirm our prediction, we examined excitation-power-dependent Raman scattering spectra as shown in Fig. 4(a). According to previous studies, the frequency at $\sim 580$ nm can be assigned to $A_1$(LO) mode.\(^{11,12}\) As described above, the internal strain arises from the built-in surface electric field through the converse piezoelectric effect. We can clearly see a low-frequency shift of $A_1$(LO) peak mode in the Raman scattering spectra due to the enhanced strain relaxation when the excitation intensity is increased. It is found that in thinner nanorods, the amount of peak shift is larger than that in thicker nanorods. As a consequence, this result further confirms the fact that the photoelastic effect does depend on the diameter of ZnO nanorods.

In order to have a more quantitative description of the Raman spectra, the magnitude of the strain in ZnO nanorods was estimated according to the induced phonon shift by the following expression:\(^{13}\)

$$
\varepsilon_{ia} = \frac{(a - a_0)/a_0}{2 \left( a_3 - b_3 \frac{C_{13}}{C_{33}} \right)},
$$

where $\Delta \omega$ is the deviation in frequency of the $A_1$(LO) phonon, $a$ and $a_0$ are, respectively, the strained and unstrained lattice constants of ZnO crystals, $a_3$ and $b_3$ are the phonon deformation potential parameters, $C_{13}$ and $C_{33}$ are the elastic constants, and $\varepsilon_{ia}$ is the biaxial strain in the $c$-plane. The frequency shift $\Delta \omega$ of ZnO nanorods (relative to the relaxed ZnO film with the peak position at 573 cm$^{-1}$, however, the spectrum is not shown here) was obtained by the Raman scattering spectra as shown in Fig. 4(a), and the parameters $C_{13} = 90$ GPa, $C_{33} = 196$ GPa, $a_3 = -690$ cm$^{-1}$, and $b_3 = -940$ cm$^{-1}$ were taken from previous reports.\(^{14,15}\) Figure 4(b) shows the $A_1$(LO) mode frequency and the biaxial strain ($\varepsilon_{ia}$) in our measured samples as a function of the excitation power. Clearly, the compressive biaxial strain in the $c$-plane of nanorods decreases with increasing excitation power; moreover, we can clearly see that the thinner ZnO nanorods exhibit a larger relaxation of biaxial strain.

In conclusion, we demonstrated the size dependence of the photoelastic effect in ZnO nanorods. The underlying origin of the photoelastic effect has been firmly confirmed arising from charged surface defects, through the converse piezoelectric effect. It is found that the thinner rods will exhibit a more pronounced effect due to a larger surface to volume ratio. Our study shown here can be extended to many other nanoscaled materials. The research along the guideline shown here should be very useful for the application of nanoscaled semiconductors in optical modulators.

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