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Photoelastic effect in ZnO nanorods

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Abstract

A novel phenomenon called the photoelastic effect had been observed in ZnO nanorods, along with a number of intriguing anomalies. With increasing excitation power, it was found that the A_1 (LO) phonon exhibited a red-shift in frequency, on top of a blue-shift in the photoluminescence (PL) peak energy. In addition, the temperature-dependent photoluminescence spectra behaved quite differently under high and low excitation power. All our results can be accounted for by the photoelastic effect, in which the built-in surface electric field was screened by photoexcited electrons and holes. Through the converse piezoelectric effect, the internal strain was therefore altered. Our results make possible a new thrust for manipulating the physical properties of ZnO nanorods, and should prove very useful in the application of optoelectric devices.

1. Introduction

Due to the combination of a large bandgap of 3.3 eV as well as piezoelectric properties, ZnO already has numerous industrial applications [1]. Compared with other wide bandgap semiconductors such as GaN, ZnO is widely available in fairly high-quality bulk and also much simpler crystal-growth technology exists, resulting in potentially lower costs for ZnO-based devices [1, 2]. Another prominent feature of ZnO is its large exciton binding energy (60 meV) [1], which holds the promise for producing efficient room-temperature exciton emitters and very low-threshold lasers. Recently, one-dimensional nanoscale ZnO has attracted a considerable amount of research interest as a prime candidate for nanoscale optoelectronics applications such as photodetectors [3], light-emitting diodes [4], and lasers [5]. Additionally, gas sensors based on nanoscale ZnO exhibit a high sensitivity and fast response due to the large surface-to-volume ratio [6]. In this paper, we outline the discovery of a phenomenon called the photoelastic effect in ZnO nanorods [7–9], along with several intriguing anomalies. With increasing excitation power, the A_1 (LO) phonon mode was red-shifted in frequency, on top of a blue-shift in the micro-photoluminescence (μ -PL) spectra. Also, the PL spectra exhibited drastically different temperature dependences under low and high excitation power. All of our results can be accounted for by the photoelastic effect.

The photoelastic effect is defined as an external electromagnetic wave capable of producing a change in the internal strain of a material [7]. It is well known that ZnO is a piezoelectric material [1, 10], in which an electric field

can induce a strain, and vice versa. Oxygen defects are also known to exist on the surface of ZnO [11, 12], giving rise to the possibility that electrons can be trapped, thereby creating a surface electric field. This process results in an upward band bending near the surface. Through the converse piezoelectric effect, ZnO nanorods therefore contain an internal stress. With the intrinsically large surface-to-volume ratio characteristic of nanostructures, the modulation of the surface electric field can have a significant influence on the physical properties of the ZnO nanorods. For instance, after photon excitation, the spatially separated photoexcited carriers can screen the built-in electric field, which in turn changes the internal strain and leads to the so-called photoelastic effect [7–9]. As a consequence, one would be able to manipulate the physical properties of ZnO nanorods via an external light beam, a trait that is extremely useful for the application of optoelectric devices based on ZnO nanorods.

2. Experiment

ZnO nanorods were grown on *a*-plane sapphire substrates via the vapour–liquid–solid process [13]. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM 6500 system. The μ -PL and μ -Raman scattering measurements were all performed at room temperature in a backscattering geometry using a Jobin Yvon T64000 system working in the triple-subtractive mode. The incident and scattered light propagated parallel to the *c*-axis, which in turn was normal to the growth surface. The sample was excited by a continuous wave (cw) He–Cd laser working at 325 nm, and a

Figure 1. Scanning electron microscopy images of nanorods (a) top-viewed and (b) viewed at a tilt angle of 20° ZnO.

Figure 2. Excitation power dependence of the photoluminescence spectra.

neutral density filter was used to control the laser intensity. In addition, a relaxed ZnO film with the *c*-plane facet grown on a sapphire substrate was used as a reference sample [14].

3. Results and discussion

As shown in figure 1, the ZnO nanorods that were studied were well aligned along the *c*-axis on a sapphire substrate. The ZnO nanorods form a well-organized hexagonal shape with a diameter of 90–160 nm, and a length of about 2 μm. Figure 2 shows the excitation-power-dependent PL spectra of (a) ZnO nanorods and (b) ZnO film at room temperature. The excitation power was varied from 4 to 160 W cm⁻², and the spot size of the laser was focused to about 40 μm². The ultraviolet (UV) emission was attributed to the exciton transition [1]. It is clear that with increasing excitation power, the increase in the peak energy of the ZnO nanorods could be as large as 10 meV, while that of ZnO film remained the same. This result implies 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.

The excitation-power-dependent Raman scattering spectra were also performed with a laser spot size of 40 μm², as shown in figure 3. In order to analyse the spectra, we first review the selection rules. The space group symmetry of the

Figure 3. Excitation-power-dependent Raman scattering spectra of ZnO film (dotted line) and ZnO nanorods (solid line).

wurtzite-type ZnO belongs to C_{6v}^4 with two formula units in the primitive cell. Group theory analysis predicts that the optical phonons at the Γ point of the Brillouin zone would be classified as $1A_1 + 2B_1 + 1E_1 + 2E_2$ [15]. Among these, the A_1 and E_1 modes are both Raman and infrared active, and they are polar and split into transverse optic (TO) and longitudinal optic (LO) phonons. The two nonpolar E_2 modes (E_{2H} and E_{2L}) are Raman active only, and the B_1 modes are infrared and Raman inactive (silent modes). As shown in figure 3, the Raman spectra were recorded with the incident light parallel to the *c*-axis in the backscattering geometry. In this configuration, A_1 (LO) and E_2 are the only allowed modes for the wurtzite-type ZnO crystals according to the Raman selection rules, and all other modes are forbidden [15, 16]. Thus, the frequencies at ~ 580 and ~ 330 cm⁻¹ are respectively assigned to the A_1 (LO) and multiple-phonon process modes for both samples [17]. It is clear that the frequencies of the A_1 (LO) and multiple-phonon process modes of the ZnO nanorods are respectively higher and lower than that of ZnO film at the same excitation power. As described above, the internal strain arises from the built-in surface electric field through the converse piezoelectric effect. Interestingly, for the ZnO nanorods, it was observed that the A_1 (LO) mode decreased in frequency while the multiple-phonon process mode followed an opposite trend, i.e. these two modes approached the corresponding modes respectively in relaxed ZnO film. The frequency shift of the multi-phonon process mode was rather small, implying that it might have been caused by a complex process involving more than one phonon. On the other hand, these modes were almost unchanged with increasing excitation power in the ZnO film (not shown here). This result can be easily accounted for in terms of the photoelastic effect [7–9]. Upon light illumination, the surface electric field is screened by photoexcited electron–hole pairs, and the internal strain is reduced. Therefore, the phonon modes tend to move closer to those of the relaxed ZnO film. For the ZnO film, because the surface to volume ratio is much smaller than that of the ZnO nanorods, the photoelastic effect is negligible. It is worth noting that photoelastic effect

Figure 4. Raman shift and the strength of the biaxial strain as a function of the excitation power.

has been studied previously in ZnO bulk [8, 9]. Unlike our study show here, in order to have a large enough strain, an external acoustic wave has to be applied.

In order to have a quantitative explanation, the strength of the strain in the ZnO nanorods was estimated according to the induced phonon shift by the following expression [18]:

$$\varepsilon_{aa} \equiv (a - a_0)/a_0 = \Delta\omega / 2 \left(a_\lambda - b_\lambda \frac{C_{13}}{C_{33}} \right), \quad (1)$$

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_λ and b_λ are the phonon deformation potential parameters, C_{13} and C_{33} are the elastic constants, and ε_{aa} is the biaxial strain in the c -plane. The frequency shift $\Delta\omega$ of ZnO nanorods (relative to the relaxed ZnO film) was obtained by the Raman scattering spectra as shown in figure 3, and the parameters $C_{13} = 90$ GPa, $C_{33} = 196$ GPa, $a_\lambda = -690$ cm⁻¹, and $b_\lambda = -940$ cm⁻¹ were taken from previous reports [19, 20]. Figure 4 shows the A_1 (LO) mode frequency and the biaxial strain (ε_{aa}) as a function of the excitation power. The deviation in frequency demonstrated that a biaxial compressive strain in the c -plane and hence a uniaxial tensile strain along the c -axis both existed in the ZnO nanorods. With increasing excitation power, the value of ε_{aa} increased from -1.0% to -0.5% , which implied a reduced biaxial compressive strain as well as a reduced uniaxial tensile strain in the nanorods [19, 20].

Through the photoelastic effect, the internal strain decreases with increasing excitation power, and it is known that the decrease in the biaxial compressive strain will result in a reduced transition energy of the exciton [20]. However, the PL peak energy of the ZnO nanorods increased with increasing excitation power, as shown in figure 2(a), and it was quite subtle that the PL peak energy was much lower than that of the relaxed ZnO film. We believe that this behaviour is due to the fact that the surface-to-volume ratio of nanorods is much larger than that of the epilayer, and the surface effect on nanorods must be taken into account. As described above, there exists a built-in electric field and band bending near the surface of ZnO nanorods. The upward band bending will create an electron depletion region near the surface and therefore reduce

Figure 5. Schematic diagram of the band energy of ZnO nanorods under (a) low and (b) high optical excitation power.

Figure 6. Photoluminescence peak energy as a function of temperature under different excitation powers.

the bandgap energy, as shown in figure 5(a). Upon optical excitation, the photoexcited electrons and holes are swept in opposite directions by the built-in electric fields. The electrons accumulate at the centre of the nanorods, while the holes get confined at the surface and neutralize the negatively charged states. Upon further increasing the 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 increases to E_{high} , as shown in figure 5(b). Based on the above argument, the increased PL peak energy from low to high excitation power is attributed to the reduced band bending effect. Therefore, we can see that both of the anomalies in the Raman scattering and PL spectra can be explained quite well by the interplay between the built-in electric field, the piezoelectric effect, and the photoexcited electrons and holes.

Finally, figure 6 shows the PL peak energy of the ZnO nanorods as a function of temperature under different excitation powers. A PL blue-shift was observed in the case of low excitation power in the low-temperature region, whereas for high excitation power the temperature dependence followed a monotonic trend. Based on the above discussion, we conclude that the PL blue-shift under low excitation power at low temperature was caused by the thermally induced screening of the built-in electric field. Since carriers frozen in the trapping centres at low temperature would be thermally

activated with increasing temperature, they would be able to screen the built-in electric field, and hence the PL peak energy would increase. The temperature-dependent PL peak energy thus reflected a competition between the blue-shift induced by thermal screening and the red-shift induced by electron–phonon interaction. As temperature exceeded about 50 K, the electron–phonon interaction dominated and the PL peak energy decreased with increasing temperature. On the other hand, for high excitation power the screening effect was already exhausted by photoexcited electrons and holes, which thus led to the observed monotonic temperature dependence.

4. Conclusion

In conclusion, a novel photoelastic effect has been observed in ZnO nanorods. With increasing excitation power, the screening of the built-in electric field gave rise to a decrease of the upward band bending and a reduction in the internal stress. Consequently, the PL peak energy exhibited a blue-shift and the A_1 (LO) phonon mode decreased in frequency. Besides, we can also thermally vary the built-in electric fields through the screening of the piezoelectric effect in the ZnO nanorods. Our results should be very useful for the application of ZnO-based nanoscale optoelectronic devices, and they can also be extended to the study of other nanostructured semiconductors.

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