Rapid Communication

Brillouin scattering study on elastic and piezoelectric properties of laser irradiated ZnO single crystals*

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Brillouin light scattering technique can be successfully used to determine the whole set of elastic and piezoelectric constants of a ZnO single crystal irradiated by different laser energy densities, into a micron range (radiation layer thickness). It is found that the scattering intensity, the linewidth and the Brillouin scattering shift of acoustic phonons are all strongly dependent on laser energy density. Based on the sound propagation equations and these results, the directional dependences of the compressional and shear moduli of the irradiated ZnO sample in the (001) plane are investigated. It is found that under an appropriate laser condition, 248 nm KrF excimer laser irradiation can significantly improve the surface quality and increase the elastic properties of ZnO single crystal. This procedure has potential applications in the fabrication of ZnO-based surface acoustic wave and optic-electronic devices.

Keywords: laser irradiation, ZnO single crystal, Brillouin scattering
PACC: 6220D, 6320, 7210D

1. Introduction

ZnO has recently attracted much attention because of its fundamental physics significance and the potential applications for ultraviolet (UV) and blue light emitting devices.[1−4] ZnO is also one of the key materials in surface acoustic wave devices, piezoelectric and pyroelectric devices, and gas sensors. For the theoretical investigation and the efficient design of these devices, it is important to have the fundamental material parameters including elastic, piezoelectric, and dielectric constants. The complete set of material property data will provide not only the necessary data needed for device design using this crystal system, but also bases for further theoretical study on the principle of the domain engineering process.

Brillouin scattering (BS) is a powerful tool to investigate elastic properties of materials without contact.[5,6] Sound velocities and thus elastic stiffness constants can be determined in a high accuracy. Such a complete set of the constants for the purity ZnO single crystals was determined by other researchers through using a hybrid method of combining ultrasonic and resonant techniques,[7,8] as well as BS.[9] It was recently found that under an appropriate laser condition, 248 nm KrF excimer laser irradiation could significantly improve the structure and the optical properties of GaN.[10−12] To our knowledge, the effects of laser irradiation on elastic stiffness and piezoelectric constants of ZnO crystals have not been studied by means of Brillouin scattering. In the present paper, BS measurement is carried out for a bulk ZnO single crystal to determine the whole set of the elastic stiffness and piezoelectric constants. The results are compared with those reported previously and also discussed.

2. Experiment

Plates were cut from the inner part of the purity ZnO crystal bulk, in the direction perpendicular to the growing axis (0001) by hydrothermal method. Two (0001) faces of the plate for all samples used here were polished to optical quality and cleaned by chemical cleaning method. The plates were irradiated with a 248 nm KrF laser at room temperature. The laser energy density was controlled from 100 to 600 mJ/cm^2 with a repetition rate of 4 Hz. Further details of the laser irradiation system were described elsewhere.[13] Three samples, each with a size of 5 mm×5 mm×0.5 mm irradiated separately at 0, 200 and 450 mJ/cm^2, are selected for BS experiments. Back scattering configuration sketched in Fig. 1 was

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used to obtain the complete set of elastic and piezoelectric constants from only one crystal sample. The relationship between sound velocity V and the Brillouin scattering frequency shift $\Delta\nu$ can be determined by these scattering geometries. For example, with a back scattering (180° scattering), $V = \Delta\nu/q$, where q is the phonon wave vector $4\pi n/\lambda$ with n being the refractive index of the crystal and λ the wavelength of laser. The refractive indices of ZnO used here were measured by the minimal angle deviation method.[14] The refractive indexes of the three samples used here were determined to be 2.52, 2.53 and 2.51 for the wavelength of 514.5 nm, respectively.

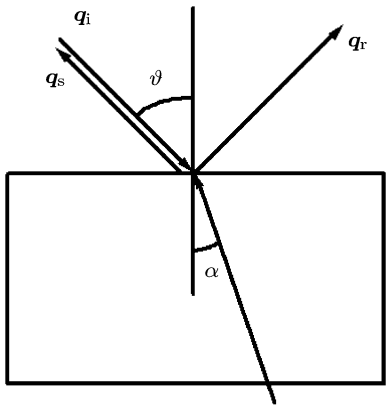


Fig. 1. Geometry of acousto-optic interaction in the backscattering condition where $\boldsymbol{q}_i$, $\boldsymbol{q}_s$, and $\boldsymbol{q}_r$ are the wavevectors of incident, scattered and reflected phonons, respectively.

The scattering light was analysed by a six-pass tandem Fabry–Perott interferomenter, detected by a photon counting photomultiplier, and input into a multichannel scaler. Based on the sound propagation equations and the measured velocity data, a full set of elastic, piezoelectric and dielectric constants can be determined. In order to observe the longitudinal acoustic phonon (LA) and two transverse acoustic phonons (TA1 and TA2) the polarization of scattered light was not analysed in the experiment. A computer-based nonlinear least-square fitting method was developed in order to accurately obtain the numerical values of elastic, piezoelectric and dielectric constants and to ascertain their signs.

3. Results and discussion

The equation of motion of a plane wave propagating in a piezoelectric material can be as written as[15,16]

$$\rho V_{\boldsymbol{q}}^2 u_i = \Gamma_{ijkl} q_j q_l u_k, \qquad (1)$$

where $V_{\boldsymbol{q}}$ is the velocity of the acoustic phonon propagating with wave vector $\boldsymbol{q}$ in the directional cosines $\boldsymbol{q}_j$ and $\boldsymbol{q}_l$ the u_i and u_k denote the displacements (polarization) of the wave, $\rho = 5.69$ g/cm^3 is the density of ZnO single crystal, and Γ_{ijkl} is the piezoelectrically stiffened elastic modulus:

$$\Gamma_{ijkl} = C_{ijkl}^E + [(e_{rij}q_r)(e_{skl}q_s)/(\varepsilon_{mn}^s l_m l_n)]\,. \qquad (2)$$

Here, C_{ijkl}^E is the elastic stiffness modulus in constant electric field, e_{rij} and e_{skl} are the piezoelectric stress constants, and ε_{mn}^s is the permittivity at constant strain, whereas l_m and l_n are the directional cosines of the wave propagation direction. For the ZnO crystal with a wurtzite structure (6 mm), there are five independent elastic stiffness constants (C_{ijkl}), and $C_{12} = C_{11} - 2C_{66}$ labeled as C_{11}^E, C_{33}^E, C_{12}^E, C_{13}^E, C_{44}^E and C_{66}^E in Voigt notation, as well as three independent piezoelectric constants e_{15}, e_{31} and e_{33}. Table 1 shows the relationships between the measured parameters, ρV^2, (ρ is the density of ZnO) and the corresponding electro-elastic constants, the directions along which the velocities were measured and the corresponding Brillouin scattering geometries. From Table 1, two elastic constants, C_{33}^E and C_{44}^E can be determined directly by measuring one LA and two TA phonon velocities along [001] in backscattering. In order to obtain the remaining independent constants and piezoelectric coefficients, Brillouin scattering in platelet geometry was employed to determine velocities from quasi-longitudinal, quasi-transverse, and transverse waves within the (001) plane for an arbitrary propagation direction. Using the sound velocity measured by Brillouin scattering method in (001), the elastic and the piezoelectric coefficients of ZnO were calculated by combining algebraic computations with a computer-based nonlinear least-squares fitting method. A complete set of elastic, and piezoelectric constants measured and derived from the samples n1 to n3 are shown in Table 2. Taking the errors in experiment and computation into account, the uncertainties in the elastic and the piezoelectric coefficients are both about 5%. The anisotropies of the measured elastic constant and piezoelectric constant determined in this work for the sample n1 are similar to those reported in the literature[7] as shown in Table 2. However, only one sample was needed in this work for the determination of a complete set of the electro-elastic and piezoelectric constants by Brillouin scattering. It is obvious that sample n1 differs from samples n2 and n3 in elastic constant as shown in Table 2. That is, the

values obtained from the measured velocity of sample n2 irradiated at 200 mJ/cm^2 are shown to be 3% higher than those of the sample n1. On the contrary, those values of the sample n3 decrease with laser energy density increasing up to 450 mJ/cm^2 and reduce about 5% compared with those of the sample n1. This discrepancy can be explained based on the difference in laser energy density between each other and indicates that structural and optical properties of the surface layer on ZnO crystal are significantly affected by the laser energy density.

Table 1. Acoustic phonon modes and sound velocities for ZnO. ρ is the crystal density.

scattering geometries	propagation directions	mode	sound velocity
backscattering	$Q//[001]$	LA	$\rho V^2 = C_{33}^{\rm E} + e_{33}^2/\varepsilon_{33}^s$
		TA1	$\rho V^2 = C_{44}^E$
		TA2	$\rho V^2 = C_{44}^{\rm E}$
platelet geometry	Q//[sinθ, 0, cos θ]	quasilongitudina	$V_{\rm LQ}^{\rm a}$
		quasitransvers	$V_{\rm TQ}^{\rm b}$
		transverse	$\sqrt{\dfrac{c_{66}\sin^2\theta + C_{44}\cos^2\theta}{\rho}}$

[a] $\rho V_{QL}^2 = (c_{11}\sin^2\theta + c_{33}\cos^2\theta + c_{44})/2 + \sqrt{[(c_{11}-c_{44})\sin^2\theta - (c_{33}-c_{44})\cos^2\theta]^2/4 + (c_{13}+c_{44})^2\sin^2\theta\cos^2\theta}$.
[b] $\rho V_{QT}^2 = (c_{11}\sin^2\theta + c_{33}\cos^2\theta + c_{44})/2 - \sqrt{[(c_{11}-c_{44})\sin^2\theta - (c_{33}-c_{44})\cos^2\theta]^2/4 + (c_{13}+c_{44})^2\sin^2\theta\cos^2\theta}$.

Table 2. Elastic coefficients/GPa and piezoelectric coefficients/(C/m^2).

	as-grown	200 mJ/cm^2	450 mJ/cm^2	Ref. [7]	Ref. [8]	Ref. [9]
$C_{11}^{\rm E}$	206±10.3	212.11±10	195.3±9.8	207	209.7	190
$C_{12}^{\rm E}$	116.86±5.8	120±6	111±5.6	117.7	121.1	110
$C_{13}^{\rm E}$	107±5.4	110.2±5.5	101.65±5.1	106.1	105.1	90
$C_{33}^{\rm E}$	208.7±10.4	209.65±10	209.72±10	209.5	210.9	196
$C_{44}^{\rm E}$	43.9±2.2	45.2±2.3	41.7±2.1	44.8	42.47	39
$C_{66}^{\rm E}$	44.57±2.2	46±2.3	42.3±2.1	44.6	44.29	40
e_{15}	–0.45±0.02	–0.44±0.02	–0.45±0.02	/	/	/
e_{31}	1.22±0.06	1.23±0.06	1.21±0.06	/	/	/
e_{33}	–0.53±0.03	–0.52±0.03	–0.53±0.03	/	/	/

Ultrasonic pulse technique (Ref. [7])
Ultrasonic resonance method (Ref. [8])
Brillouin scattering spectroscopy (Ref. [9])

Figure 2 shows that the orientation dependences of compressional and shear moduli of the ZnO crystal irradiated at 200 mJ/cm^2 in (100) plane, in which solid lines represent the angular dependences of ρV^2 for different modes can be calculated, and open circles represent experimentally measured data in the first quadrant. It turns out that the velocity of the compressional (LA) mode is strongly dependent on orientation. It follows from Fig. 2 that its velocity reaches a maximum along the [001] propagation direction, and it decreases to a minimum in the [011] direction The velocities of the first shear (TA1) mode do not change at all for different propagation directions. On the other hand, the velocities of the second shear (TA2) mode change significantly with propagation direction. The TA1 and the TA2 modes represent the shear waves propagating in the same (001) plane with their particle displacements perpendicular to the plane. The TA2 mode has a maximum velocity in [011] and a minimum velocity in [001], which indicates the presence of a 'soft shear acoustic mode' in [100] of ZnO.

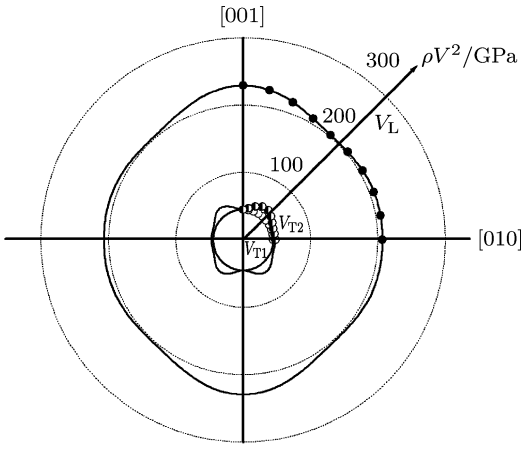


Fig. 2. Measured values of ρV^2 for the compressional (LA) and two shear modes (TA1 and TA2) in the (100) plane of ZnO single crystal irradiated at 200 mJ/cm^2.

Figure 3 shows Brillouin spectra obtained for a fixed backscattering angle $\theta = 45°$ on the surface of the ZnO samples irradiated by different laser energy densities. It can be observed that one of the two well defined peaks at lower frequencies corresponds to the transverse acoustic phonons (TA1), the other one, whose position is dependent on B according to Eq. (2), is a quasitransvers (QTA). The third peak present at a larger frequency in the spectrum of Fig. 2 corresponds to the bulk quasilongitudinal acoustic wave (QLA). It is found that both the intensities and the bandwidths of the acoustic phonons including QLA, TA1 and QTA modes vary with laser fluence. The Brillouin spectrum of the laser treated-ZnO sample can be improved slightly under an appropriate laser condition compared with that of the sample n1. Among them, the sample n2 irradiated at 200 mJ/cm^2 reveals the strongest scattering intensity and the narrowest full width at half maximum (FWHM). Brillouin scattering intensity is highly sensitive to the surface state of the sample. It has been known that excimer laser irradiation on the surface of sample under an appropriate condition can induce the interdiffusion of surface atoms and eliminate structural defects such as vacancies. In our experiments, when the samples are irradiated under an appropriate laser energy in air, some oxygen atoms can be adsorbed onto the surface , thereby occupying those positions of oxygen vacancies. The surface of the laser treated-ZnO becomes more stoichiometric with the reduction of the oxygen vacancies. As a result, laser irradiation under an appropriate condition can improve the crystal quality on the surface of ZnO, so that the shifts of both the scattering intensity and Brillouin scattering of the laser treated-ZnO sample increase. On the contrary, sample n3 irradiated by 450 mJ/cm^2 gradually reduces the scattering intensity and broadens the FWHM, as well as the peaks of the acoustic phonons shift toward lower frequency as shown in Fig. 3. These features indicate that too high a laser fluence can induce the surface damage of ZnO, which is probably due to laser ablation effect, produce structural defects such as interstitial zinc, oxygen vacancies and interstitial oxygen or zinc vacancies induce tensile stress over the irradiated layer during irradiating, then lead to the reductions in Brillouin scattering intensity and elastic and piezoelectric constants of sample n3 irradiated at 450 mJ/cm^2.

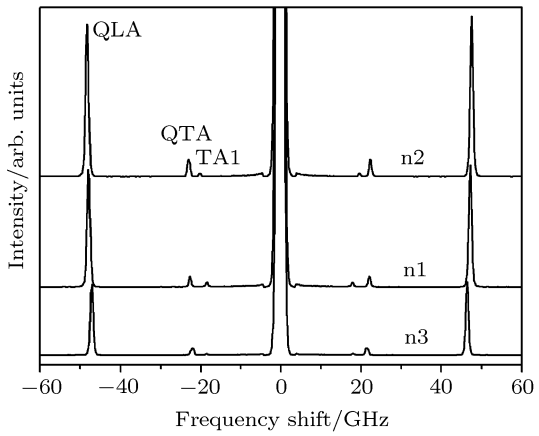


Fig. 3. Brillouin spectra for a fixed backscattering angle $\theta = 45°$ on the surface of the ZnO samples irradiated at different values of laser energy density (E_i), where n1 represents un-irradiated sample, n2 denotes 200 mJ/cm^2 irradiated sample, and n3 refers to 450 mJ/cm^2 irradiated sample.

4. Conclusion

We have measured the effects of 248 nm KrF excimer laser irradiation on the Brillouin light scattering spectra of ZnO single crystals irradiated by different laser energy densities. The whole set of elastic and piezoelectric constants of a single ZnO crystal irradiated at different laser energy densities is determined, in a micron range (irradiation layer thickness). The data obtained by the asgrown ZnO crystal are similar to those previously determined from four samples by Brillouin scattering techniques. Based on the sound propagation equations and these results, the directional dependences of compressional and shear moduli of the irradiated ZnO samples in the (001) plane are investigated. It is found that under an appropri-

ate laser condition, 248 nm KrF excimer laser irradiation can significantly improve the surface quality and increase the elastic properties of ZnO single crystal. This procedure has potential applications in the fabrication of ZnO-based surface acoustic wave and optoelectronic devices.

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