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To cite this article: Dickson Mwenda Kinyua et al 2019 Nanotechnology 30 305201

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Received 18 January 2019, revised 25 March 2019
Accepted for publication 8 April 2019
Published 1 May 2019

Abstract
In this work, we present an experimental study on the acoustic vibrations of ZnO nanoparticles array with different concentration of Ga dopings by using femtosecond pump-probe technique. The Ga-doped ZnO (GZO) nano-triangle particles with the sizes of 190, 232 and 348 nm are fabricated by nanosphere lithography and pulsed laser deposition method. The result indicates that the frequency of acoustic vibrations of GZO nanoparticles decrease as the Ga-concentration is increased. Importantly, the vibration period of the GZO nanoparticles at the same Ga doping concentration show a nonlinear increase as the nanoparticle size is increased, which is different from the common linear dependency in undoped ZnO nanoparticles. It may be attributed to the crystal structure distortion and elastic characteristics variation due to Ga doping, and the elastic modulus at 7.3% Ga doping is decreased by 30%–60% for GZO nanoparticles with different sizes. The study can be very helpful for evaluating the crystal structure distortion and elastic characteristics of doped nano-materials with optical methods. Besides, it can offer a complementary method of thermal management in ZnO based optoelectronic devices.

Keywords: GZO, acoustic vibrations, nanoparticle arrays, crystal structure distortion

1. Introduction
The interest in ZnO nanostructures continues to grow due to its unique properties that make them attractive for application in nano-devices. ZnO has a wide bandgap, large exciton binding energy (60 meV) at room temperature [1], is biosafe and biocompatible [2]. It is used in various photonic devices such as LEDs, lasers and room temperature polariton lasers [3–5]. To further enhance the performance of the ZnO nano-devices, the material is often doped to alter the intrinsic properties. Various dopants such Mg [6], N [7], Al [8] and Ga [9–11] have been used, but Ga offers various advantage such as: close atomic radius of Ga and Zn, leading to minimal strain and local lattice distortion [12, 13] and increased transparency in the visible region [14]. However, much of the work done on the effect of Ga doping of ZnO (GZO) is based on static techniques such as UV–vis, Raman and x-ray. Therefore, it is necessary to study the dynamic properties of GZO to determine the carrier’s behavior such as electron–phonon interactions, and their effect on materials properties.

Pump-probe spectroscopy is a powerful time-resolved approach for studying excited state dynamics in nano-materi-\[\text{els}^{,}\text{owing to its high temporal resolution [15]. The pump laser excite the carriers in materials. Then energy relaxation and electron–phonon interaction leads to some strain in the materials, which is monitored by probe laser. It has been widely used to study the dynamics of coherent phonons in various material systems, including metals, semiconductors and heterostructure forms [16–18]. Specifically, it has also been used to characteristic the coherent acoustic phonons (CAP) in c-ZnO epitaxial film [19] and the interaction of CAPs and polariton states in 0.5 mm thick c-ZnO single crystal [20]. Additionally, pump-probe spectroscopy has become a key to non-destructive apprehension of the...\]
mechanical properties in nanostructures [21–23]. This all-optical time-resolved method is also among the go-to techniques to characterize interfacial thermal transport at the nanoscale, which is important for optoelectronic nanodevices.

So far, a lot of research work about the coherent acoustic vibrations have been done on the effects of periodic modifications of nanostructures. Moreover, a variety of factors can also influence the vibrations, such as type of substrate [24–26], periodicity of the nanoparticles, aspect ratio and so on [27]. In fact, doping in the nanomaterials can also lead to influence on the acoustic vibrations due to the crystal structure distortion and elastic properties change. However, the effect of doping on the coherent vibrations of nanostructures is seldomly reported. Herein, for the first time we report a detailed study on the influences of Ga doping on the acoustic vibration in GZO nanoparticle arrays by using femtosecond pump-probe technique. It indicates that the frequency of acoustic vibrations of GZO nanoparticles decrease as the Ga-concentration is increased. Importantly, the vibration period of the GZO nanoparticles at the same Ga doping concentration show a nonlinear increase as the nanoparticle size is increased, which is different from the common linear dependency in undoped ZnO nanoparticles. It may be attributed to the crystal structure distortion and elastic characteristics variation due to Ga doping, and the elastic modulus at 7.3% Ga doping is decreased by 30%–60% for GZO nanoparticles with different sizes. The study can be very helpful for evaluating the crystal structure distortion and elastic characteristics of doped nano-materials with optical methods. Besides, it can offer complementary way of thermal management in ZnO based optoelectronic devices.

2. Experimental details

The GZO nano-arrays were fabricated on mask templates by pulsed laser deposition (PLD) method with KrF excimer laser (Lambda Physics, 330 mJ, 248 nm repetition rates of 5 Hz). GZO films were also deposited on silicon substrates under the same condition to compare with the nano-triangle particle arrays [13]. The mask templates for nano-arrays were prepared on the cleaned substrates using polystyrene spheres with diameter of 820, 1000 and 1500 nm (Duke Scientific Corporation) by nanosphere lithography (NSL) method. After the deposition by PLD, the samples were ultra-sonicated in alcohol for 30 s to clean up the polystyrene spheres and GZO nano-arrays. To get arrays or films, the deposition by PLD, the samples were ultra-sonicated in methanol for 30 s to clean up the polystyrene spheres and GZO nano-arrays. The probe wavelength is 800 nm, generated by a second harmonic BBO crystal, and was focused through an 8 cm lens onto the surface of the GZO films or nano-arrays. The probe wavelength is 800 nm, which is delayed in time to the pump and is focused onto the same position of the sample through an objective lens (20×). To collect the reflected probe beam from the sample surface, a balanced photodiode detector (Thorlabs, PDB210A/M) connected by a lock-in amplifier (Stanford, SR830) is used.

3. Results and discussion

Figures 1(a)–(c) show AFM images of GZO nanoparticle arrays. The figures indicate uniformly distributed periodic nano-triangle particles. The bisector lengths of the nano-triangles were about 190 nm, 232 nm and 348 nm, respectively. AFM images of the ZnO nano-film at different Ga doping levels of 0%, 2.9% and 7.3% are shown in figures 1(d)–(f), respectively. The images show smooth surface in all the samples. The RMS of the nano-film reduced from 17.6 to 2.9 nm with Ga doping concentrations increased from 0% to 7.3%.

To determine the crystal structure distortion in ZnO introduced by Ga doping, we compare the XRD patterns of GZO at different Ga doping concentrations, see figure 2(a). The results revealed that all the samples have a sharp peak at 2θ = 34.460°, corresponding to ZnO (002) plane. This implies that the samples maintain the hexagonal wurtzite crystal structure. For the 7.3% Ga2+ doped sample, (110), (100) and (101) crystal planes are also observed though (002) plane remains superior. Besides, it was observed that the (002) peak position shifted from 34.460° to lower values with increase in Ga concentrations, as shown in table 1. This indicates relative strain in ZnO nano-arrays due to Gallium doping [29].

Additionally, we obtained the change in full wave half maximum (FWHM), and the average crystalline size (D_{hal}) as doping levels was increased, (where the change in FWHM and D is defined as FWHW/D_{hal(Ga doped GZO)}–FWHD/ D_{hal(0% doped GZO)}). Table 1 show that the FWHM increases with increasing Ga concentration, meaning that the crystalline size reduced. The crystalline size of the GZO nano-film can be calculated using Debye Scherer equation [30] [D_{hal} = k\lambda/(\beta\cos\theta_{hal})] where k is a constant (k = 0.89), \lambda is the wavelength of XRD with Cu-Kα radiation (\lambda = 0.154 06 nm) and \beta is the FWHM in radians of the (002) diffraction peak. From the table it is concluded that increasing the Ga contents leads to decrease in D_{hal}. Besides, we calculate the internal strain (\varepsilon) introduced in the crystal using
the expression:

\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]  

where \( \beta \) is the FWHM and \( \theta \) is the diffraction angle [31]. The calculation results show increased strain in the films with increasing Ga concentration (see table 1).

Figure 2(b) shows the UV–visible transmission spectra of the GZO arrays deposited at different concentrations of Ga in 200–900 nm range. All the spectra show a sharp absorption edge in the region between 300 and 400 nm, which shifts depending on the doping. The shifting of the absorption edges could have been caused by doping induced Burstein–Moss effect. Similar results were obtained for GZO films deposited by spray pyrolysis [32].

In the pump-probe spectroscopy experiments, to observe the change in the acoustic vibrations in GZO nanoparticles, 400 nm pump laser beam was used to excite the electrons.
from the valence band to the conduction band by two photon absorption (TPA) or one photon absorption via the deep levels such as Zn-interstitials and Zn-vacancies [33]. Additionally, acoustic phonons may be induced by thermal and electronic stress created by pump pulse. Figures 3(a)–(c) show the differential reflectance (−ΔR/R) traces upon exciting the GZO nano arrays with different sizes at 2.9% of Ga concentration. Since the single photon energy of the pump laser was below the band gap $E_g$ of ZnO, there is a small dip around the zero decay time attributed to TPA [34]. The TPA was followed by an immediate positive turn which is attributed to band filling effect. Finally, through the electron–phonon scattering thermalization and other relaxation mechanisms, the excited electrons decay exponentially. Interestingly, there was a dip on the decay for the undoped arrays as shown by an arrow in figure 3(d) because of band-gap renormalization (BGR) effects [35]. However, Ga doping concentration increasing in ZnO particles results in surface defects increasing [36] and therefore may induce the diminished effect of the BGR.

The $-\Delta R/R$ can be expressed as a complex product of the Gaussian function $[g(t)]$ and a multi-decay function $(M_t)$ as follows $-\Delta R/R = g(t) \otimes M_t$ [37]. $M_t$ is the sum of the electronic and phonon relaxation contribution. We first study the electronic relaxation effects $(R_e)$ as a result of doping. The red continuous line in figure 3 shows the fitting of the $R_e$ by the below formula [38]:

$$R_e = A_1 \exp \left( \frac{t}{\tau_1} \right) + A_2 \exp \left( \frac{t}{\tau_2} \right) + A_3 \exp \left( \frac{t}{\tau_3} \right)$$

A1, A2 and A3 are the scaling factors whereas, $\tau_1$, $\tau_2$ and $\tau_3$ represents the ultrafast, fast and slow lifetime constants respectively. The ultrafast and fast process can be attributed to the recombination of carriers at the defects. The slow decay could be set down to electron–phonon coupling and electron–hole recombination. Similar result was obtained for Molybdenum doped ZnO nanocrystalline thin films [39] and aluminium doped ZnO thin films [31].

To investigate the acoustic vibration in GZO nanoparticle arrays, we separate the background contribution of the excitons to the nanoparticles to obtain the residual traces, see the insert in figures 3(a)–(d). After applying a fast Fourier transform (FFT), a spectrum with a distinctive peak frequency for each array is obtained as shown in figures 4(a) and (b) for undoped and 7.3% doped GZO respectively. The black, red and blue represent the 190 nm, 232 nm and 348 nm particles respectively. There is a decrease in frequency as the particles size become larger for all doping concentrations. The vibrations in the nanotriangles can be attributed to radial breathing modes ($f$ inversely proportional to particle size) and edge modes along the boundaries [40]. Figure 4(c) shows the relationship between the nano-triangle particle size and the periodic time of the acoustic vibration at various doping concentrations. The periodic time of the vibrations increased with the array size.

For the undoped ZnO nanoparticles, the dotted line shows the linear fitting, see in figure 4(c). We note that the line passes through zero which indicates the propagation stress from silicon substrate does not impact the vibrations oscillation [18]. The frequency of the nano-triangle arrays can be defined as follows [41, 42]:

$$\frac{1}{f} = \frac{2a}{v},$$

where $f$ is the frequency, $v$ is the longitudinal sound velocity in bulk and $a$ is bisector length of the triangular nano-arrays. Comparing the equation (3) and linear fit ($T = 3.3775a \times 10^{-4}$), a longitudinal sound velocity of 5921.5 ± 0.9 $\text{m/s}$ is obtained from the gradient. This is slightly lower than the velocity in bulk ZnO [19]. This demonstrate the effect of periodic boundary conditions on the phonon dispersion using triangular nanoparticles. Using relations $v_g = \sqrt{C/\rho}$ [43] where $v_g = 5921.5$ ± 0.9 $\text{m/s}$ is longitudinal sound velocity, $C$ is the elasticity and $\rho = 5606 \text{kg/m}^3$ is the mass density for ZnO. We obtain a elasticity value of 196.6 ± 6 GPa which is within 111.2 ± 4.7 $\text{GPa}$ and 310 ± 40 GPa for single crystal [44] and epitaxial layers [45] ZnO respectively using spherical nanoindentation.

However, once the dopants are introduced, the vibration period show an unusual nonlinear increase with the particle size increase, for GZO arrays of the same doping concentration (figure 4(c)). Several factors such as the periodicity of the nanoparticles and the substrate effect can contribute to this nonlinear effect as pointed in the introduction. However, since all the samples were prepared under the same experimental conditions, we conclude that the effect of doping had a major impact on the unusual change of vibration period in our experiments. We suggest that for the GZO nanotriangles with larger size which have higher aspect ratio, the possible frequency shift contributed from surface acoustics effects [27], might be increased with the doping effect. As earlier discussed, Ga-doping introduced distortions and strain in the crystal structure of ZnO could account for the variations that are observed in these doped nano-triangle array samples. Figure 4(d) shows that the elasticity (C) value decreased with increase in Ga concentration and size of the nano arrays. This is mainly attributed to the corresponding reduction in the vibration frequency as both the Ga concentration increased and array size become bigger.

To verify that indeed the frequency of the acoustic vibrations in ZnO is affected by crystal distortions as a result of Ga doping, we measured the time-resolved spectroscopy of the GZO nano-films deposited under the same condition. Figure 5(a) shows the FFT graph of the nano-films at different

<table>
<thead>
<tr>
<th>Doping level (%)</th>
<th>2θ peak position (°)</th>
<th>Change in FWHM (°)</th>
<th>Change in $D_{lat}$ (nm)</th>
<th>Internal strain $\varepsilon \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>34.460</td>
<td>—</td>
<td>—</td>
<td>4.705</td>
</tr>
<tr>
<td>2.9</td>
<td>34.227</td>
<td>0.650</td>
<td>-0.4669</td>
<td>4.830</td>
</tr>
<tr>
<td>5.0</td>
<td>34.159</td>
<td>3.863</td>
<td>-2.5643</td>
<td>5.299</td>
</tr>
<tr>
<td>7.3</td>
<td>34.094</td>
<td>6.225</td>
<td>-3.8703</td>
<td>5.645</td>
</tr>
</tbody>
</table>

*The negative in $D_{lat}$ suggests smaller $D_{lat}$ value to undoped sample.
Ga concentrations, which shows the oscillation frequency reduces with increase in doping. The peak frequencies were 30.4 GHz, 28.5 GHz, 24.0 GHz and 19.3 GHz for GZO films with different Ga concentrations of 0%, 2.9%, 5% and 7.3%, respectively. Using Thomsen’s model, the oscillation frequency can be expressed as follow [46, 47]:

\[ f = \frac{nvk_{\text{probe}}}{\pi} \]

where \( k_{\text{probe}} = \frac{2\pi}{\lambda} \) is the wave number of probe beam (\( \lambda = 800 \text{ nm} \)), \( n \) is the refractive index, and \( v = 6200 \text{ ms}^{-1} \) is the sound velocity of ZnO [19]. A refractive index value of 1.97 is obtained, which is close to the reported value of 1.9597 [48]. And we analyze the FFT signals peaks in figure 5(a) (see the insert in figure 5(a)). The peak frequencies follow the expected eigen modes frequency sequence \( f_m = m(v/2d) \), with \( m = 1, 2, 3, \ldots \) and \( v \) is the longitudinal sound velocity and \( d \) the nano-film thickness which is \( \sim 90 \text{ nm} \). So we confirm that the oscillation is attributed to an acoustic pulse generated at the film surface and travelling back and forth across the surface. The acoustic phonon frequencies of the material is a factor of the material properties according to the elasticity theory \( (v\sqrt{E/\rho}) \) where \( E \) is the Young’s modulus and \( \rho \) is the mass density [49]. Though the Ga impurity changes the \( \rho \), it is unlikely to significantly influence the frequency of the vibrations alone because the difference between the Zn and Ga atom mass is small (factor of 1.0664). Another factor which can also affect the frequency of the oscillation is the atomic radius difference. The difference in the atomic radius leads to lattice distortions [36] and influence on the phonon velocity and refractive index [50].

Interestingly, the plots of the frequency and internal strain against the doping concentration clearly show the relationship between them (figure 5(b)). Whereas the frequency showed a decrease as the doping level was increased, the opposite was for the internal strain. Since the frequency varies proportionally to \( E \) and inversely proportionally to \( \varepsilon \), it can be concluded that the reduction of the oscillation frequency could be attributed to the increased strain as a result of doping. Generally, the acoustic phonons play a dominant role in heat transport and thermoelectric properties of semiconductor nanostructures; therefore it is interesting to assess its implication of doping. Kargar et al [50] explained the relationship between the scattering rates \( (1/\tau, \text{ where } \tau \text{ is the phonon lifetime}) \) and the introduction of dopants at low temperature where the Umklapp scattering is minimal. They showed \( 1/\tau \) was proportional to the concentration of foreign atoms, atomic radius and mass of the host and foreign atoms. This fundamentally implies that the introduction of Ga dopants could alter the thermal conductivity of the ZnO by changing the scattering rates. Thus, in GZO nanoparticles, similar crystal structure distortion and strain will be
Figure 4. (a) and (b) show fast Fourier transform of the acoustic vibration in GZO nano-particle arrays of undoped and 7.3% Ga concentration respectively. The bisector lengths of the arrays are: 190 nm, 232 nm and 348 nm in black, red and blue respectively. (c) Shows the relationship between the acoustic vibration and the nano-particle arrays size at various doping concentrations. The dotted line shows the linear fitting for the 0% GZO nano-particle arrays. (d) Shows the variation of the elasticity ($C$) with doping at different Ga doping levels.

Figure 5. (a) FFT of the acoustic phonons oscillation (black-0%, blue-2.9%, red-5% and green-7.3% doped). Insert, breathing frequency oscillation modes of undoped and doped GZO (b) relationship between the oscillation frequency peak and the internal strain introduced as a result of Ga doping.
introduced by Ga doping. This could alter the thermal conductivity of GZO nanoparticles, which can affect the vibration phonons frequency.

4. Conclusion

In summary, the dynamic properties of the charge carriers and the acoustic vibration in GZO nanoparticles were studied by using pump-probe experiments with varying the Ga doping concentration. The acoustic vibration frequency excited in the GZO nanoparticles of the same size decreased as the doping concentration increased, which was attributed to the internal strain in the crystal introduced by doping. Additionally, the oscillation period in GZO nanoparticles shows nonlinear increase as the size is increased, which is different from the linear increase on sizes in undoped ZnO particles. The results are helpful for evaluating the crystal structure distortion and elastic characteristics of doped nano-materials with optical methods.

Acknowledgments

This work was supported by National Natural Science Foundation of China (nos. 11774115, 91850113), the 973 Programs under grants 2014CB921301, and the Doctoral fund of Ministry of Education of China under Grant No. 20130142110078. Special thanks to the Analytical and Testing Center of HUST and the Center of Micro-Fabrication and Characterization (CMFC) of WNLO for using their facilities.

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