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Ultrafast time-resolved spectroscopy of ZnSe nanowires: Carrier dynamics of defect-related states

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ABSTRACT

In recent years, ZnSe nanowires have been widely investigated for their potential applications in opto-electronics. A typical room temperature photoluminescence spectrum of ZnSe nanowires grown by vapor–liquid–solid growth under different growth conditions shows that the spectrum is dominated by two characteristic emission peaks. The first peak is attributed to the band edge emission peak at 2.68 eV whereas the second to the broad deep defect-related emission peak in the region of 1.8–2.4 eV. In this work, we present a study of ultrafast time-resolved spectroscopy of defect states of ZnSe nanowires grown under Se-rich growth conditions. We investigate in detail the carrier dynamics of these nanostructure materials using selective optical excitation femtosecond pulses from a wavelength tunable optical parametric amplifier system. The effects of intrinsic point defects inherent in the manufacturing of these materials and in particular the relaxations of the photogenerated carriers occupying these defect states are examined. Temporal dynamics on a few picoseconds time-scale provided information on effects such as state filling and secondary excitation and their contribution to the overall induced absorption. Long time-scale probing of induced absorption provided information on the defect states associated with the observed photoluminescence in this material.

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1. Introduction

The realization of light emitting semiconductor devices in the blue region of the spectrum has been the objective of many research groups over the past decade [1–3]. A number of research groups worldwide are focusing their efforts on II–VI semiconductors due to their relatively large bandgap energy. Of particular interest from this group of semiconductors is ZnSe which has a direct bandgap of 2.7 eV at room temperature. However, one significant problem with this material has been the difficulty in obtaining stoichiometric crystals, even at optimum growth conditions, and as a consequence, such crystals consist of high concentration of defects. Unfortunately these defects limit the ability of using this material in the development of light emitting devices. Attempts to synthesize this material in lower dimensions, such as nanowires, with the objective to reduce the concentration of these defects have not been very successful. These nanowires, when subject to different growth conditions, have photoluminescence spectra that are dominated by two characteristic emission peaks – namely, a narrow band edge emission peak centered at 2.68 eV and a much broader deep defect-related emission peak in the region of 1.8–2.4 eV. It was found that the presence of the broad low energy luminescence peak is attributed to intrinsic point defects of the ZnSe lattice [4]. Recently, there has been a significant development in band edge emission control in this material [5]. It was demonstrated that nanowires grown under Zn-rich conditions are dominated by strong band edge emission, while nanowires grown under Se-rich conditions have strong defect-related emission. In view of the complexity of ZnSe nanowires and the dependence of their optical properties on growth conditions, it is essential to obtain a better understanding of the fundamental processes and interactions in these nanostructure materials under different growth conditions. Although there have been numerous studies using photoluminescence, there has been relatively little work on understanding the ultrafast relaxation mechanisms in these materials [6] and in particular the short relaxation dynamics of the defects states.

Ultrafast carrier dynamics in semiconductors have been investigated using excitation-probe techniques over the past decades [7], providing important information on the design and development of efficient high speed electronic and optical devices. In this work, the results of ultrafast carrier dynamics in defects of ZnSe nanowires which are energetically placed within the bandgap energy of this nanostructure material are presented. ZnSe nanowires grown by vapor–liquid–solid growth (VLS) mechanism under Se-rich growth

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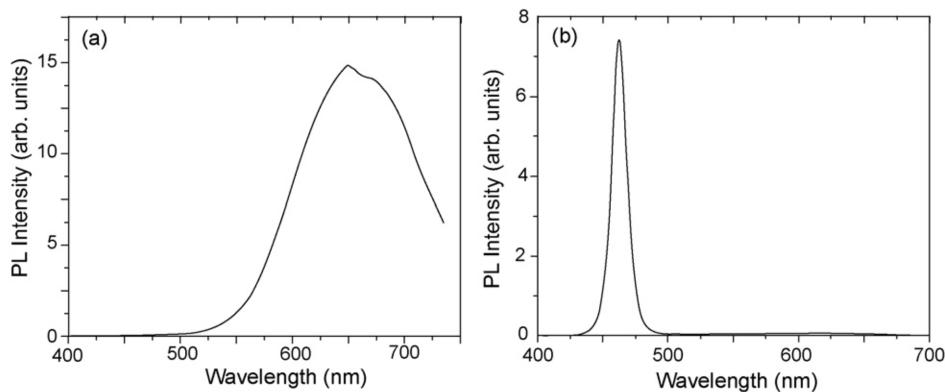

Fig. 1. Photoluminescence measurements for ZnSe nanowires grown under Se-rich (a) and Zn-rich (b) conditions.

conditions with a large number of defects states as well as Zn-rich grown samples have been studied. The different relaxation time constants as well as the sign of the induced absorption for these samples, suggest that point defects play a crucial rule in the relaxation of the photogenerated carriers on a picosecond time-scale.

2. Experimental details

Here, the dynamical behavior of ZnSe nanowires following ultrashort pulse excitation is investigated through a transient combination of reflectivity and transmission. The source of excitation consists of a self mode-locked Ti:Sapphire oscillator generating 100 fs pulses at 800 nm. A regenerative amplifier system is used to amplify the pulses $\sim 10^6$ times at a repetition rate of 1 kHz. These pulses were used as the source of excitation of an optical parametric amplifier generating short pulses below the bandgap of ZnSe in the wavelength range of 480–730 nm. These ultrashort pulses are used in a non collinear pump-probe configuration. The temporal variation in optical absorption was monitored as a change in the reflectivity and transmission, which provides a direct measure of the photo-excited carrier dynamics within the probing region [8]. In this work, optical absorption fluence of $\sim$0.5 mJ/cm^2 has been used to excite the ZnSe nanowires and determine its temporal behavior.

The nanowires were grown on silicon (1 1 1) *n*-type substrates using vapor phase growth, based on the Au-catalyzed VLS mechanism, [9]. The growth temperature for the sample was maintained at 650 °C. The nanowires have diameters in the range of 80–100 nm and lengths of 8–10 μm. The nanowires were deposited on quartz substrates with a typical density of about 10^4 wires/mm^2 to perform the measurements reported in this work. Finally, we should point out that characterization of these samples can be found in detail elsewhere [5]. Photoluminescence measurements for the ZnSe nanowires grown under Se-rich and Zn-rich conditions are shown in Fig. 1.

3. Results

Degenerated transient absorption measurements of the Se-rich grown ZnSe nanowires, following ultrafast excitation below the bandgap are shown in Fig. 2. This figure depicts the temporal behavior over a series of pump-probe wavelengths ranging between 480 and 730 nm corresponding to probing defects states with energies below the bandgap for the nanowires grown under the conditions described above. Similar measurements carried out for Zn-rich grown sample reveal no detectable induced absorption. The estimated photogenerated carrier density was approximately 8×10^{19} carriers/cm^3 for the fluence used in this work. Here, we should point out that measurements were also carried out at carrier densities up to three times less than the above, and still showed similar relaxation rates and with linear peak signal dependence. The absorption changes for ZnSe nanowires grown under Se-rich conditions seen in Fig. 2 cover a range of several picoseconds following excitation at $t = 0$. What is interesting here is that we have observed three different temporal behaviors corresponding to three excitation wavelength regions. The first region corresponding to wavelengths 486–510 nm, where there is an increase in absorption, a fast rise followed by a much slower recovery toward equilibrium. In the second wavelength range between 520and 570 nm the transient absorption change was very small and not observable even at the highest fluence used in this work. Finally, the third range covers the spectral region 587–730 nm where the transient change was negative. Table 1 shows the fast recovery of the induced absorption signal extracted through a single exponential fit to the corresponding experimental data.

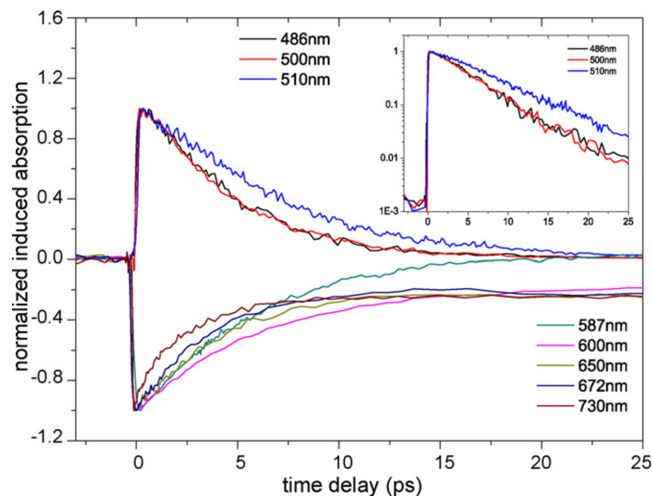

Fig. 2. Normalized time-resolved induced absorption of defect states within the bandgap for ZnSe nanowires grown under Se-rich conditions. The sample is excited and probed using an ultrafast optical parametric amplifier. The inset shows some of the data on a semi-log scale to demonstrate the exponential behavior.

Fig. 3 shows the degenerated transient induced absorption measurements for a range of different excitation fluences between 0.25 and 2 mJ/cm^2 at 650 nm wavelength. Initially, there is a linear increase in the induced absorption from 0.25 to 1 mJ/cm^2, whereas with further increase of the fluence there is a saturation in the signal. Here, we should point out that the temporal recovery in

Table 1
Relaxation times for Se-rich ZnSe nanowires for the degenerated pump-probe measurements discussed in the text.

Wavelength (nm)	Relaxation time (ps)
486	5.3
500	5.2
510	7.6
587	5.8
600	6.1
650	4.3
672	3.5
730	2.7

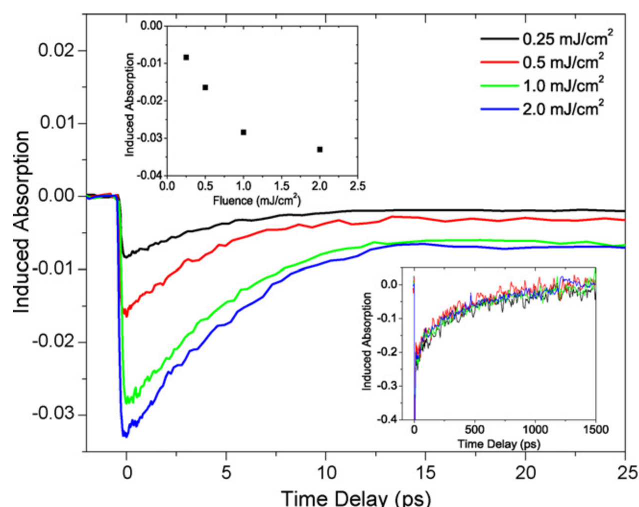

Fig. 3. Degenerated time-resolved induced absorption of defect states within the bandgap for ZnSe nanowires grown under Se-rich conditions at 650 nm for different excitation fluences between 0.25 and 2 mJ/cm^2. Upper inset shows the peak induced absorption as a function of fluences. The lower inset shows the normalized induced absorption changes in a long-time window of 1.5 ns.

short time-scale of the induced absorption change becomes slightly slower with increasing the fluence. The inset of Fig. 3 shows the normalized induced absorption changes in a long-time window of 1.5 ns. Clearly evident is that for all fluences the recovery on this time-scale is the same.

4. Discussion and analysis

Excitation of a semiconductor material, with ultrafast laser pulses, whose photon energy is larger than the bandgap energy, will result in the generation of electron–hole pairs. These photogenerated carriers will undergo several stages of energy relaxation and spatial redistribution that can be temporally resolved using a variation of ultrafast excitation-probe techniques. In a defect free semiconductor material, below bandgap excitation (for excitation fluences smaller than that where non-linear effects become important) will not result in a generation of carriers thus there will not be any noticeable absorption change in the material properties. However, in a semiconductor such as the Se-rich grown ZnSe nanowires there are a large number of defect states generated within the bandgap energy (2.7 eV). As a result of the existence of these defects there will be absorption of photons corresponding to the energy of these states resulting in the generation of carriers. These photogenerated carriers will result in altering the “steady-state” absorption of the material through affects such as, state filling (SF) [10] or free carrier (FC) induced absorption [11] to higher energy states. SF is a consequence of the occupied available energy states by the photogenerated carriers resulting in a time dependant reduced absorption whose temporal dependence depicts the relaxation of these carriers out of the probing energy states. Carriers generated in these defect energy states within the gap may also undergo secondary excitation to a higher energy state resulting in an increased absorption. The amplitude of this absorption will depend on the coupling efficiency between these energy states and the number of carriers present in the lower coupled energy states. Both effects, namely SF and FC are competing effects and may occur at the same time.

The time-resolved measurements (Fig. 2) performed on the Se-rich ZnSe nanowires clearly show both effects mention above. For the wavelength range of 486–510 nm there is an increase in the

Table 2
Relaxation times for Se-rich ZnSe nanowires for the degenerated pump-probe measurements at 650 nm wavelength and different excitation fluences.

Fluence (mJ/cm^2)	0.5	1	2	3
Fast relaxation time (ps)	4.2	4	4.4	5.6
Slow relaxation time (ps)	326	340	393	408

temporal absorption due to secondary excitation of the photogenerated carriers. In this probing energy region the defect-related states may be efficiently coupled to higher energy states overcoming SF effects. Here, it is interesting to point out that for all these probing energy states the carriers have a fast recovery to the equilibrium value. The relaxation toward equilibrium is of the order of a few picoseconds as seen in Table 1. The transient absorption changes in the second range of probing wavelengths between 520and 570 nm were very small and not detectable. This may be due to absence of energy states within this probing region or most likely due to the competing effects of SF and FC.

The third range of probing energy states covers the range above 587 nm where we notice a negative change in absorption. This behavior is clear evidence of what we referred to as SF. At all probing energy states we notice a relatively fast single exponential relaxation toward equilibrium which occurred in a few picosecond time-scale (see Table 1). At the longer probing wavelengths the slow recovery toward equilibrium indicates that the photogenerated carriers occupy these energy states for a longer time. For this reason, degenerated time-resolved measurements performed with a translation stage of 25 cm travel range indicated (see inset in Fig. 3) that the residual carriers remain in these energy states for ∼0.4 ns (see Table 2). This suggests that these energy states are more likely contributing to the observed photoluminescence in this material. This result additional supports the observable luminescence peak in Fig. 1(a).

To further understand the carrier dynamics following ultrafast pulse excitation for the energy states related to the observable luminescence we have performed fluence dependent measurements. Fig. 3 shows a typical behavior of absorption change in this spectral region at probing wavelength of 650 nm. For the lower fluence we notice a linear dependence of the maximum induced absorption (see upper inset in Fig. 3), as expected from SF effect. A linear increase in fluence will result in a linear increase of the carriers occupying the energy states and as a consequence increase linearly the SF signal. The observed fast recovery is a single exponential decay and is approximately of 4 ps. A further increase in fluence results in an observed saturation as one would expect from saturation of the occupied states (see Table 2). The slight increase in the single exponential recovery may be due to the large number of photogenerated carriers which may take longer time to reach the relaxation energy state.

5. Conclusions

In this work, we have investigated the carrier dynamics of the defect-related states in ZnSe nanowires grown under Se-rich conditions. We have performed degenerated time-resolved absorption measurements and have observed three distinct probing energy regions, corresponding to 486–510 nm, 520–570 nm and 580–730 nm associated with SF and FC effects. The initial recovery of the photogenerated carriers in these energy states is of the order of 4–5 ps. The smaller energy probing defect-related states appear to have a long recovery time constant of the order of 0.4 ns which is more likely associated with the luminescence states of the material. No detectable transient induced absorption signal was observed for the Zn-rich grown sample due to the lack of defect-related states in

this material. Finally, this ultrafast carrier dynamics study provides important insight into the role that defects-related states play in the observed photoluminescence emission of ZnSe nanowire samples.

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