Phonon-assisted anti-Stokes lasing in ZnTe nanoribbons

Zhang, Qing; Liu, Xinfeng; Muhammad Iqbal Bakti Utama; Xing, Guichuan; Sum, Tze Chien; Xiong, Qihua

2015

Zhang, Q., Liu, X., Muhammad Iqbal Bakti Utama, Xing, G., Sum, T. C., & Xiong, Q. (2016). Phonon-assisted anti-Stokes lasing in ZnTe nanoribbons. *Advanced Materials*, 28(2), 276-283. doi:10.1002/adma.201502154

<https://hdl.handle.net/10356/140573>

<https://doi.org/10.1002/adma.201502154>

This is the accepted version of the following article: Zhang, Q., Liu, X., Muhammad Iqbal Bakti Utama, Xing, G., Sum, T. C., & Xiong, Q. (2016). Phonon-assisted anti-Stokes lasing in ZnTe nanoribbons. *Advanced Materials*, 28(2), 276-283, which has been published in final form at <https://doi.org/10.1002/adma.201502154>. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

DOI: (Please add manuscript number)

Article type: Communication

Phonon-assisted Anti-Stokes Lasing in ZnTe Nanoribbons

By Qing Zhang, Xinfeng Liu, Muhammad Iqbal Bakti Utama, Guichuan Xing, Tze Chien Sum, and Qihua Xiong**

[*] Dr. Q. Zhang, M. I. B. Utama

Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

Dr. X. F. Liu, Dr. G. C. Xing and Prof. T. C. Sum,

Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371;

Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, 50 Nanyang Drive, Singapore 637553;

Singapore-Berkeley Research Initiative for Sustainable Energy, 1 Create Way, Singapore 138602, Singapore.

Email: tzechien@ntu.edu.sg

Prof. Q. H. Xiong

Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371;

NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, 639798

Email: Qihua@ntu.edu.sg

Keywords: Zinc telluride; exciton-phonon coupling; anti-stokes emission; upconversion lasing; laser cooling;

Emission of molecules or semiconductors usually shifts to lower energy compared with excitation energy, which is called Stokes shift. Recently, anti-Stokes emission or upconversion has drawn considerable interests for its promising technological applications in optical refrigeration, frequency up-converted laser, biological imaging, high capacity data storage, three-dimensional micro-fabrication, photodynamic therapy and solar cells. Till now, anti-Stokes emission has been realized in a variety of materials or structures such as rare-earth element doped glasses, quantum wells, dye molecules and semiconductors.^[1-9] Several energy transfer mechanisms have been proposed to account for the anti-Stokes emission: excited states absorption (ESA, **Scheme 1a**), energy transfer upconversion (ETU, **Scheme 1b**), two-

photon absorption (TPA, Scheme 1c), phonon-assisted anti-Stokes photoluminescence (PA-ASPL, Scheme 1d).^[2, 4] ESA uses intermediate real electronic states to absorb two photons sequentially to create a highly excited carrier, which are widely involved in rare-earth element doped glasses and semiconductors with defect states. Alternatively, the anti-Stokes conversion mechanism for ETU is similar as Auger effect involving energy transfer from an excited electron-hole pair to another carrier, which is also supported in rare-earth element doped glasses and semiconductor heterostructures.^[10, 11] However, the two types of photon upconversion have some limitations with respect to the requirement of real electronic intermediate states. TPA is a simultaneous absorption of two photons *via* a virtual intermediate state to achieve an excited state.^[1, 12] TPA induced emission exhibits a large anti-Stokes shift and breaks the limitation of excitation source energy without the need for real intermediate states.^[12] However, to maintain the efficient two photon pumped emission, high-density excitation ($10^3 - 10^6$ KW cm⁻²) is required to ensure that the second photon arrives in a very short time scale (within less than a nanosecond) and absorbed by the excited electron on the virtual state.^[12] Therefore the cross section of the third-order process TPA is several orders lower than the linear upconversion absorption.

Phonon-assisted anti-Stokes emission involves indirect optical transitions mediated by the annihilation or creation of one or multiple phonons, which therefore provide opportunities to realize light-induced cooling.^[13, 14] In polar semiconductors, exciton is strongly coupled to optical phonons through Fröhlich interactions or deformation potential interactions, which is manifested by the observation of high-order Raman peaks in resonant conditions.^[15, 16] Due to the presence of strong exciton-phonon coupling in polar semiconductors, PA-ASPL can be generated at a very low excitation power. The semiconductor optical cooler based on the anti-Stokes excitonic resonance is promising for breaking the temperature limit in rare earth element doped materials imposed by Boltzmann distributions, and potential integration with

present Si technology.^[17-19] However, laser cooling of semiconductors has been attempted for decades in III-V semiconductor quantum wells without success due to external poor luminescence efficiency and strong background absorption until the recent groundbreaking work of laser cooling by 40 Kelvin on II-VI cadmium sulfide nanoribbons states.^[20, 21]

Phonon-assisted anti-stokes photoluminescence is not only useful for all-solid-state optical cooler, but also promising for manufacturing high-power self-cooled and radiation-balance lasers.^[22, 23] In conventional solid-state lasers, the Stokes shifts between the excitation photon and emission photon generate considerable amount of heat to gain materials, leading to the reduction of output power and beam quality or even structure damage to gain materials. While, in the proposed self-cooled and radiation-balanced lasers, anti-Stokes emission is proposed to mitigate the heating effect. The output power of laser operated with the radiation-balanced technique can be much higher than the conventional laser. Inorganic II-VI and III-V polar semiconductors are good gain materials and widely used in commercial solid-state continuous-wave and pulsed lasers.^[22-26] A further study on the radiation-balanced lasing in the polar semiconductor would be interesting for fundamental research on the anti-Stokes emission in lasing status and applications for improving the performance of the exothermic lasers.

ZnTe is a typical II-VI semiconductor with a direct band gap of 2.26 eV (548 nm) at room temperature.^[27] ZnTe has unique advantages in nonlinear and THz optics compared with other II-VI semiconductors.^[28, 29] Previously, we demonstrated a strong exciton-LO coupling strength in ZnTe nanoribbons and nanorods, leading to the emission of tenth order LO (10th-LO) phonons as well as the increasing of the exciton radiative rate.^[16, 27] Herein, we report the observation of phonon-assisted spontaneous ASPL and lasing in undoped polar II-VI semiconductor ZnTe nanoribbons as a result of strong exciton-phonon coupling. Power-dependent spontaneous emission spectroscopy and Z-scan nonlinear absorption measurements

suggest that the upconversion is due to two photon absorption with excitation wavelength λ_{ex} of 600-800 nm while phonon-assisted ASPL become dominant as λ_{ex} approach to electronic band-gap (~540 nm). The upconversion lasing threshold reduces by 80% as λ_{ex} decreases from 800 nm to 545 nm, which is attributed to the occurrence of phonon-assisted ASPL lasing. The co-exsisting of phonon-assisted anti-Stokes and two-photon pumped lasing shown in our results makes it possible for the realization high-power readiation-balanced laser in II-VI polar semiconductors. The demonstration of amplified PA-ASPL in ZnTe exhibits unconventional implications to optical refrigeration, particularly important for pushing solid-state laser cooling to lower temperatures.

Figure 1a shows a typical scanning electron microscopy (SEM) image of the as-grown nanoribbons. The detailed crystal structure characterizations can be found from our previous work.^[27, 30] Solid state lasers with output wavelength at 532 nm ($\lambda_{\text{ex}} = 2.331$ eV) and 543 nm ($\lambda_{\text{ex}} = 2.283$ eV) are used as excitation sources to probe the spontaneous emission of the ZnTe nanoribbons (experimental section). Since the excitation energy is larger than the band gap of ZnTe (548 nm, 2.263 eV) at room temperature, the ZnTe nanoribbons were cooled down to finite temperatures to probe the anti-Stokes photoluminescence. In our previous work, temperature-dependent Stokes photoluminescence measurements were conducted with an excitation of a 2.622 eV (473 nm) line of an Ar^+ ion laser to obtain the exact value of band-gap at different temperature and exciton dynamics.^[27] Based on the results, the two sample temperatures T of 220 K and 120 K are selected to probe the Stokes emission and anti-Stokes emission respectively when the excitation wavelength is 532 nm (Fig. 1b). When $T = 220$ K (blue curve, Fig. 1b), an emission band centered at 538 nm (2.313 eV) can be seen in the Stokes side of the excitation line (green arrows indicates, Fig. 1b), which is in good agreement with the PL spectra measured using 473 nm laser. Stokes first-order LO (1LO, $\varpi = 25.4$ meV) and second-order LO (2LO, $\varpi = 50.8$ meV) can be resolved above the

emission band. When the ZnTe nanoribbon is cooled down to 120 K (red curve, Fig. 1b), the emission band blue shifts and locates at the anti-Stokes side (528 nm, 2.357 eV), suggesting the occurrence of anti-Stokes photoluminescence. When the excitation wavelength is 543 nm (red arrow indicates, Fig. 1c), the anti-Stokes and Stokes PL can also be seen when the nanoribbon temperature is 215 K (blue curve, Fig. 1c) and 293 K (red curve, Fig. 1c).

The upconversion is not due to a two-photon absorption in moderate laser power, concluded from the linear dependence on excitation power of the anti-Stokes luminescence below 1200W/cm² (red dots, Fig. 1d).^[20] In higher pumping power, the output power shows a nonlinear (nearly quadratic) dependence on the excitation laser power. There are two reasons responsible for that: 1) with the formation of Te single crystal on the nanoribbon surface due to optical chemistry, non-radiative channel builds as a result of surface states^[16]; 2) two-photon absorption effects become dominating. Both of the non-radiative emission and two-photon absorption lead to heating of samples, suggested by the redshifts of the emission peak as the pumping power is larger than ~1200W/cm² (black triangles, Fig. 1d). With the increasing of sample temperature, the exciton energy moves closer to incident photon energy, resulting in a stronger resonant effect and thus an additional increase of emission power. Therefore, the ASPL power shows an exponential increase with excitation power by a law of ~2.28 (Fig. 1d). The value is slightly larger than 2 when there is no resonant effect but only two-photon absorption is considered. However, at low pumping power the ASPL peak shows no apparent variation or slight blue shifts (black triangles, Fig. 1d) due to possible optical cooling by the annihilation of phonons in ASPL process, which is in good agreement with the phonon-assisted ASPL mechanism (Scheme 1d).

As indicated in Fig. 1b and 1c, strong sharp Raman peaks, assigned to fundamental LO (1LO), second-order LO (2LO) and transverse optical (1TO and 2TO) phonons respectively, can be resolved above broad band of Stokes and anti-Stokes luminescence

emission. As the excitation photon wavelength (532 nm, Fig. 1b; 543 nm, Fig. 1c) approaches the emission wavelength (~527–550 nm), the Stokes and anti-Stokes Raman scattering cross section of four phonon modes are enhanced because of resonant effect, or more fundamentally due to the exciton-optical phonon Fröhlich interaction.^[31] The Raman peak intensities increase with the decreasing of energy difference between the Raman scattering photons and exciton. As shown in Fig. 1b, when the excitation wavelength is 532 nm (Fig. 1b), the intensities of Stokes Raman peaks are higher than their anti-Stokes counterparts at 220 K; while at 120 K the anti-Stokes Raman peaks become stronger than Stokes counterpart, revealing that phonon annihilation rate dominates over creation rate. The same phenomenon is observed when the excitation wavelength is 543 nm (Fig. 1c). Additionally, we did not observe any emission at the lower energy side of 532 nm, suggesting that the contribution due to shallow defects is negligible thus ruling out the occurrence of ETU induced upconversion.

The occurrence of phonon-assisted ASPL process is supported by the temperature-dependent Stokes and anti-Stokes emission studies, as shown in Fig. 1e and 1f. When the temperature decreases from 135 to 40 K (Fig. 1e), the quantum efficiency therefore Stokes PL intensity of the ZnTe nanoribbon increases due to a lower activity of non-radiative transition channels associated with surface and defect states. The non-radiative transition rate is proportional to $\exp(-E_a/k_B T)$, where E_a is the activation energy and k_B is Boltzmann constant. The exciton dynamics including exciton origin and exciton recombination mechanisms have been explored previously.^[27] As shown in Fig. 1f, the Stokes PL intensity is well-fitted with a single exponential function (green curve). The intensity value is extracted from the emission spectra when the excitation wavelength is 473 nm. In contrast, the anti-Stokes emission intensity shows monotonic decrease as the further decreasing of temperature (Fig. 1f, red curve), as a result of the reduction of phonon population at lower temperature, which is also supported by experimental Raman spectra. To conclude, the linear power-

dependence of ASPL and decreased up-conversion intensity as the decreasing of temperature demonstrate that the resonant annihilation of phonons facilitates the up-conversion in ZnTe nanoribbons.

Next we explore the amplified spontaneous up-conversion emission in ZnTe nanoribbons. Five pulsed laser lines 800 nm, 680 nm, 600 nm, 550 nm and 545 nm were selected as excitation sources to pump up-conversion lasing in individual ZnTe nanoribbons. The base temperature is set at 80 K by flowing liquid nitrogen. When the excitation photon energy is far below the band gap (2.48 eV), *e.g.*, 800 nm (1.55 eV), the upconversion is dominated by two photon absorption. Figure 2a shows the optical image under white light illumination and upconversion lasing image when the excitation laser wavelength is 800 nm. The upconversion lasing image (green light) is mainly emitted from the edge of nanoribbon, suggesting the good cavity quality of the nanoribbons. Figure 2b and 2c display the evolution spectra from upconversion spontaneous emission to stimulated emission when the excitation wavelength is 800 and 550 nm, respectively. The integrated emission intensity is extracted and plotted as a function of pumping fluence (inset, Fig. 2b). When the excitation intensity is below the threshold, a broad spontaneous emission band was observed which shows a linear increase with excitation fluence (Fig. 2b and c, inset). While as the pumping power is larger than the threshold, the emission intensity shows a superlinear increase with the excitation fluence as well as the appearance of a sharp peak over the PL band indicating the occurrences of amplified spontaneous emission (Fig. 2b and 2c). As the pumping power further increases, due to the optical gain saturation, a stable lasing status is reached and the emission intensity becomes linear with excitation intensity. The evolution from spontaneous emission (linear), amplified spontaneous emission (superlinear) to lasing (linear) is reflected by an “S”-shaped power-dependent emission intensity predicted by the rate equation of multimode lasing model (inset, Fig. 2b and 2c), which has been used as hard evidence in claiming the lasing behaviors

^[32-34]. Although limited by the quality of materials and cavity, the peak width at the half maximum (FWHM) of the lasing peaks are around 1.5-3 nm, which is comparable with previous nanoribbon/nanowire lasers ($\sim 0.5-3$ nm)^[33, 35, 36] and much smaller than expected from ASE process in semiconductors (~ 10 nm)^[34, 37], supporting the realization of lasing in this case. The quality factor Q of the ZnTe nanoribbon cavity was evaluated by $Q = \lambda_m / \lambda_{FWHM}$, where λ_m and λ_{FWHM} are center value and full width at half maximum of the lasing modes (Fig. 2b-c). λ_m and λ_{FWHM} were obtained by least squares fitting of experimental data using multiple Lorentzian functions. When the excitation wavelength is 550 nm, several lasing peaks appears with $Q \sim 330$ ($\lambda_{FWHM} \sim 1.6$ nm); while under 800 nm excitation, it is hard to distinguished each closely packed optical modes and one broad lasing peak can be resolved indicating a $Q \sim 170$ ($\lambda_{FWHM} \sim 3.1$ nm). The energy loss, characterized by quality factor, is larger when the excitation wavelength is close to excitonic resonance. The quality factor increase at 550 nm may be due to cooling effect of gain materials in the presence of radiation balance (to be discussed later). Furthermore, the upconversion lasing threshold with excitation wavelength of 800 nm is 755 $\mu\text{J}/\text{cm}^2$. When the excitation photon energy increased to 2.254 eV (550 nm), the upconversion lasing threshold was significantly reduced to be 174 $\mu\text{J}/\text{cm}^2$ (Fig. 2d), about $\sim 21\%$ of that in 800 nm excitation case.

The presence of phonon-assisted anti-Stokes emission with the pulsed laser excitation is also supported by power-dependent upconversion lasing intensity analysis. Figure 2d shows the power-dependent upconversion emission intensity with the five different excitation wavelengths. As the excitation wavelength decreases from 800, 680, 600, 550 to 545 nm, the threshold reduces from 755, 570, 360, 258 to 174 $\mu\text{J}/\text{cm}^2$. To reveal the underlying physics, the relationship between spontaneous upconversion output intensity I_{out} below threshold as integrated pumping energy I_{in} is analyzed. $I_{out} = \alpha_1 I_{in} + \alpha_2 I_{in}^2$ (Fig. 2d), where α_1 , α_2 denotes one photon and two photon absorption coefficients, respectively. The linear component and

nonlinear component (quadratic term) represents the contribution from phonon-assisted ASPL and TPA process, respectively. α_1 , α_2 can be deduced from the log-log scaled $I_{\text{out}}-I_{\text{in}}$ curves in Fig. 2d. When the excitation wavelength is 800, 680 and 600 nm, the emission intensity I_{out} can be well fitted using a function as $I_{\text{out}} = \alpha_2 I_{\text{in}}^2$ where linear component α_1 is nearly zero, suggesting the dominant TPA processes. Since the TPA coefficient at 680 nm is larger than 800 nm, the upconversion lasing threshold at 680 nm is lower. As the excitation wavelength approaches 550 nm and 545 nm, the contribution of linear component, or that phonon-assisted ASPL grows. The slope of $\log I_{\text{out}}-I_{\text{in}}$ is around 1.3 and 1.1 at 550 and 545 nm respectively, which are smaller than 2 for TPA dominant condition, supporting the occurrence of phonon-assisted ASPL. The observation is consistent with the result when the excitation source is a continuous-wave laser (Fig. 1b-c).

In order to quantitatively determine the two-photon absorption coefficient of ZnTe at different wavelengths, we have also performed open aperture Z-scan measurements here. Due to the instrumentation limit, we use ZnTe crystal instead of individual ZnTe nanoribbon to extract this parameter. This approach is acceptable and reliable since the sizes of our nanoribbons in three dimensions are far beyond quantum confined regime, and therefore the two photon absorption coefficient of the nanoribbon is expected to be close to their bulk crystal counterparts. **Figure 3a** shows the open-aperture z -scan response of ZnTe single crystal at the incident intensity (wavelength 600 nm) increasing from 20 GW/cm² to 100 GW/cm². The dependence of the z -scan normalized transmittance change (ΔT) as a function of the excitation irradiance (energy ω_0 , wavelength λ) is plotted as shown in Fig. 3b. The slope derived from a linear fit (log-log scale) of ΔT as a function of excitation intensity indicates the mechanism of two-photon absorption. To directly compare the two-photon absorption coefficient at different excitation wavelength, the open aperture z -scan responses

of ZnTe crystal are measured at the incident intensity of 100 GW/cm² (Fig. 3c). The normalized transmittance of the open aperture *z*-scan can be described as

$$T_{OA} = \frac{1}{\pi^{0.5} q_0} \int_{-\infty}^{\infty} \ln[1 + q_0 \exp(-x^2)] dx, \quad [1]$$

Where $q_0 = \alpha_2 \cdot I_{00} / (1 + z^2 / z_0^2) \cdot [1 - \exp(-\alpha_0 L)] / \alpha_0$, α_0 and α_2 are the linear and two-photon absorption coefficients, respectively, I_{00} is the on axis peak power and $z_0 = \pi \omega_0^2 / \lambda$ is the Rayleigh range.^[38] From the best fitting of the data, the two-photon coefficients at different wavelength can be extracted. As the excitation laser wavelength decreases from 800 nm to 545 nm ($0.69 < h\omega_0 / E_g < 1$), the two photon absorption coefficient α_2 shows a monotonic increase. While in classic two-band model, the two photon absorption coefficient decreases as excitation wavelength approaches to edge bandgap from $0.7E_g$.^[39-41] The spectral dependence observed in our experiment may be due to 1) the presence of interband transition around critical energy in ZnTe (3.78 eV, ~328 nm and 4.34 eV, ~285 nm) and 2) near-resonance enhancement effect around energy bandgap, as reported previously.^[42, 43] The extracted absorption coefficient $1/\alpha_2$ versus excitation wavelength is plotted in Fig. 3d (black dots). To elucidate the relationship between threshold and the two-photon coefficients, these values are normalized according to the threshold value at 800 nm. As shown in Fig. 3d, the two curves show good overlap in the two-photon absorption regime (800-600 nm); while in the two photon absorption plus phonon-absorption lasing regime (for example at 550 nm), the deviation between the two curves becomes evident, suggesting the existence of the phonon-assisted ASPL.

The temperature of ZnTe nanoribbons upon laser excitation is evaluated by the emission energy. Figure 4a shows the upconversion spectra below lasing threshold which were taken at different excitation wavelength. The excited carrier density remained fixed through probing the integrated ASPL intensity with the varying of excitation wavelength. To

make the temperature analysis reliable, the carrier density was kept around one third of the lasing threshold to avoid the optical effect arising at intense excitation and introducing PL peak shifts such as band filling and band renormalization, etc. Fig. 4b shows the local temperature of ZnTe nanoribbon, evaluated by the emission wavelength extracted out from Fig. 4a. When the excitation wavelength is 720 nm, the spontaneous upconversion emission wavelength is 528.28 nm. The corresponding local temperature is 113 K, which is higher than the base temperature of 80 K due to heat generation by Stokes shifts from two-photon absorption. When the excitation wavelength approaches 570 nm, the Stokes shifts become larger thus more excess photon energy is released, which generates more heat and results in further increasing of temperature ~120 K. When the excitation wavelength is 545 nm, the spontaneous emission wavelength blueshifts to 528.2 nm, corresponding to a local temperature of 112 K, which is 8 K lower than the peak temperature at ~ 570 nm excitation. Such transition at 570 nm can only be explained by the transition from a two-photon induced photoluminescence at longer wavelengths to a dominating phonon-assisted anti-Stokes emission at short wavelengths. We consider that the heating effect in spontaneous emission is partially mitigated by phonon-assisted anti-Stokes emission.

We propose a possible amplified spontaneous phonon-assisted ASPL process: (1) As the optical injection energy is approaching lasing threshold, more and more electrons are excited to conduction band via absorbing phonons or two photons, leading to the building of population inversion; (2) A photon with energy in resonance with the exciton enters the population inverted system and stimulates the emission of additional photons in coherent with each other, which is so-called optical amplification; (3) Since the optical gain is larger than optical loss, the emission intensity increases exponentially with optical propagating distance. With the presence of optical cavity, the optical modes are selected, giving rising to the achievement of ASPL lasing. In polar semiconductors, the strong exciton-phonon coupling

and related resonant effect ensure a large cross section of ASPL stimulated emission. Now in ZnTe nanoribbons lasers, thermal energy generated by Stokes-shift is partially balanced by radiation cooling of phonon-assisted anti-Stokes emission, which extensively increase the output power and reduce the threshold of the nanoribbon laser. According to our result, the output power of radiation-balanced ZnTe laser would be much higher than exothermic type laser at the same pumping fluence. On the other hand, stimulated or amplified spontaneous PA-ASPL, counterpart of the stimulated/amplified spontaneous PL, may provide a good solution to realize efficient optical cooling in solids. With the presence of PA-ASPL lasing, the photon-absorption coefficient, the quantum yield therefore the population of annihilated phonons would increase extensively as expected, which may lead to a high cooling efficiency.

In summary, our results demonstrate that anti-Stokes photoluminescence via resonant annihilation of phonons would be a general property for polar semiconductors with strong exciton-phonon coupling. This anti-Stokes emission could be readily introduced into the other semiconductor up-conversion processes to promote the emission efficiency or effectively reduce the threshold of amplified spontaneous emissions. The lasing performance of semiconductor nanostructures is greatly improved by radiation cooling of phonon-assisted anti-Stokes emission. The first attempt of radiation-balanced lasers in semiconductors will benefits the applications in high-power laser and related opt-electronic devices. The demonstration of ASPL lasing is not only important for realizing net laser cooling in more semiconductors and even quantum emitters, but potentially could be advantageous to push down the cooling temperature in the existing systems.

Experimental Section

Synthesis of ZnTe nanoribbons:

The ZnTe nanoribbons were synthesized using a home-built vapor transport thermal evaporation method as we reported previously^[27, 30, 44-47]. In the setup, a quartz tube was mounted on a single zone furnace (Lindberg/Blue M TF55035C-1). ZnTe powder source (99.99%, Alfa Aesar) was located at the center of the quartz tube. The substrate, $\langle 100 \rangle$ p-Si chip (with native oxide) coated with a 6 nm layer of gold nanoparticles by thermal evaporating (Elite Engineers), was put inside the downstream region of the quartz tube. The quartz tube was evacuated to a base pressure of 2 mTorr, followed by a 30 sccm flow of high purity Ar premixed with 5% H₂ gas. The temperature and pressure inside the quartz tube were set and stabilized to 850°C and 50 Torr, respectively, for 90 min. The crystal structures of the ZnTe nanoribbons are characterized by scanning electron microcopy, X-ray diffraction and transmission electron microscopy (data not shown here).

Steady-state photoluminescence spectroscopy:

The as-grown sample was ultrasonicated from the growth substrate, dispersed into an isopropyl alcohol solution and drop-casted onto silicon substrates with pre-defined markers. The Stokes and anti-Stokes spontaneous emission of individual as-grown ZnTe nanoribbon was measured using a triple-grating spectrometer (Horiba-JY T64000, objective: 50×) with a backscattering geometry.^[20, 27] For low-temperature PL and Raman spectroscopy studies, the ZnTe nanoribbons are cooled by a liquid He continuous-flow microscopy cryostat (Cryo Industry of America, Inc.).^[20, 27, 44] Two solid state lasers (532 nm and 543 nm) are used to pump the ZnTe nanoribbons. The back-scattered signal was collected through a 100× objective and recorded by a liquid nitrogen cooled charge coupled device detector.

Upconversion lasing spectroscopy:

To conduct amplified upconversion emission spectroscopy, excitation pulses with wavelengths from 800 nm to 550 nm were generated from an optical parametric amplifier (TOPAS, Light Conversion Ltd), which is pumped by a 1 kHz, 150 fs Ti:sapphire

regenerative amplifier (LegendTM, Coherent, Inc).^[24, 48] A 20× optical objective was used to focus incident laser to excite the ZnTe nanoribbons; the excitation laser spot size is ~30 μm in diameter to pump the whole nanoribbon. The emission signal was collected by the same objective under backscattering configuration, and analyzed by a Princeton Instrument spectrometer.

Z-scan measurement:

Two-photon absorption coefficients of ZnTe crystal at different wavelengths were measured using the open-aperture Z-scan technique.^[38] The incident laser pulses generated from TOPAS were focused onto the sample by a lens with a 25 cm focal length, which gives a focal radius of 20 μm provided that the diameter of the collimated beam is 6 mm. The ZnTe crystal with a thickness of 0.5 mm was traversed across the focal point along the beam propagation axis.

Acknowledgements

Q. Zhang and X. F. Liu equally contributed to this work. Q.X. gratefully acknowledges strong support of this work from Singapore Ministry of Education (MOE) via an AcRF Tier2 grant (MOE2011-T2-2-051) and Tier1 grant (2013-T1-002-232), Singapore National Research Foundation through an Investigatorship grant (NRF-NRFI2015-03) and a Competitive Research Program (NRF-CRP-6-2010-2). T.C.S. acknowledges the financial support from his NTU start-up grant M4080514 and MOE Tier 2 grant MOE2013-T2-1-081. X.F.L., G.X., T.C.S. and Q.X. also acknowledge the financial support by the Singapore National Research Foundation through the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBerRISE) CREATE Programme. This work was also supported in part by United States AFOSR through its Asian Office of Aerospace Research and Development (FA2386-13-1-4112).

Reference

- [1] W. Kaiser, C. G. B. Garrett, *Phys. Rev. Lett* **1961**, 7, 229.
- [2] F. Auzel, *Chem. Rev.* **2004**, 104, 139.
- [3] M. Haase, H. Schäfer, *Angew. Chem. Int. Edit.* **2011**, 50, 5808.
- [4] A. G. Joly, W. Chen, D. E. McCready, J. O. Malm, J. O. Bovin, *Phys. Rev. B* **2005**, 71, 165304.
- [5] C. Kammerer, G. Cassabo, C. Voisin, C. Delalande, P. Roussignol, J. M. Gerard, *Phys. Rev. Lett.* **2001**, 87.
- [6] D. Kovalev, J. Diener, H. Heckler, G. Polisski, N. Kunzner, F. Koch, A. L. Efros, M. Rosen, *Phys. Rev. B* **2000**, 61, 15841.
- [7] J. Li, *Phys. Rev. B* **2007**, 75, 155315.
- [8] W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, J. C. Hummelen, *Nat. Photonics* **2012**, 6, 560.
- [9] E. Malainho, J. R. Santos, M. I. Vasilevskiy, S. A. Filonovich, Y. P. Rakovich, A. Rogach, *Phys. Status Solidi C* **2010**, 7, 1517.
- [10] T. Kita, T. Nishino, C. Geng, F. Scholz, H. Schweizer, *Phys. Rev. B* **1999**, 59, 15358.
- [11] F. A. J. M. Driessen, *Appl. Rev. Lett.* **1995**, 67, 2813.
- [12] M. Rumi, J. W. Perry, *Adv. Opt. Photon.* **2010**, 2, 451.
- [13] E. Finkeissen, M. Potemski, P. Wyder, L. Vina, G. Weimann, *App. Phys. Lett.* **1999**, 75, 1258.
- [14] M. Sheik-Bahae, R. I. Epstein, *Phys. Rev. Lett.* **2004**, 92, 247403.
- [15] J. F. Scott, R. C. C. Leite, T. C. Damen, *Phys. Rev.* **1969**, 188, 1285.
- [16] Q. Zhang, J. Zhang, M. I. B. Utama, B. Peng, M. de la Mata, J. Arbiol, Q. Xiong, *Phys. Rev. B* **2012**, 85, 085418.
- [17] M. Sheik-Bahae, R. I. Epstein, *Nat. Photonics* **2007**, 1, 693.
- [18] S. D. Melgaard, D. Seletskiy, A. Di Lieto, M. Tonelli, M. Sheik-Bahae, *Vol. 7951*, 1 ed. (Eds.: R. Epstein, M. Sheik-Bahae), SPIE, San Francisco, California, USA, **2011**, pp. 795105.
- [19] D. V. Seletskiy, S. D. Melgaard, M. Sheik-Bahae, S. Bigotta, A. DiLieto, M. Tonelli, R. I. Epstein, in *Laser Refrigeration of Solids Iii*, *Vol. 7614* (Eds.: R. I. Epstein, M. SheikBahae), Spie-Int Soc Optical Engineering, Bellingham, **2010**.
- [20] J. Zhang, D. Li, R. Chen, Q. Xiong, *Nature* **2013**, 493, 504.
- [21] D. Li, J. Zhang, Q. Xiong, *Opt. Express* **2013**, 21, 19302.
- [22] S. Bowman, C. E. Mungan, in *Advanced Solid State Lasers*, Optical Society of America, Davos, **2000**, p. MF1.
- [23] N. Galina, K. Raman, *Rep. Prog. Phys.* **2010**, 73, 086501.
- [24] X. Liu, Q. Zhang, J. N. Yip, Q. Xiong, T. C. Sum, *Nano Lett.* **2013**, 13, 5336.
- [25] Q. Zhang, G. Li, X. Liu, F. Qian, Y. Li, T. C. Sum, C. M. Lieber, Q. Xiong, *Nat. Commun.* **2014**, 5, 4953.
- [26] Q. Zhang, X.-Y. Shan, X. Feng, C.-X. Wang, Q.-Q. Wang, J.-F. Jia, Q.-K. Xue, *Nano Lett.* **2011**, 11, 4270.
- [27] Q. Zhang, X. Liu, M. I. B. Utama, J. Zhang, M. de la Mata, J. Arbiol, Y. Lu, T. C. Sum, Q. Xiong, *Nano Lett.* **2012**, 12, 6420.
- [28] Q. Wu, M. Litz, X. C. Zhang, *Appl. Rev. Lett.* **1996**, 68, 2924.
- [29] T. Bartel, P. Gaal, K. Reimann, M. Woerner, T. Elsaesser, *Opt. Lett.* **2005**, 30, 2805.
- [30] M. I. B. Utama, M. de la Mata, Q. Zhang, C. Magen, J. Arbiol, Q. Xiong, *Cryst. Growth Des.* **2013**, 13, 2590.
- [31] H. Frohlich, *Interaction of Electrons with Lattice Vibrations*, *Vol. 215*, **1952**.
- [32] L. W. Caspersen, *J. Appl. Phys.* **1975**, 46, 5194.
- [33] D. Saxena, S. Mokkaapati, P. Parkinson, N. Jiang, Q. Gao, H. H. Tan, C. Jagadish, *Nat. Photonics* **2013**, 7, 963.

- [34] J. Q. Grim, S. Christodoulou, F. Di Stasio, R. Krahne, R. Cingolani, L. Manna, I. Moreels, *Nat. Nanotechnol* **2014**, 9, 891.
- [35] C. Zhang, C.-L. Zou, Y. Yan, R. Hao, F.-W. Sun, Z.-F. Han, Y. S. Zhao, J. Yao, *J. Am. Chem. Soc.* **2011**, 133, 7276.
- [36] R. F. Oulton, V. J. Sorger, T. Zentgraf, R.-M. Ma, C. Gladden, L. Dai, G. Bartal, X. Zhang, *Nature* **2009**, 461, 629.
- [37] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* **2014**, 13, 476.
- [38] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quant. Electron.* **1990**, 26, 760.
- [39] D. C. Hutchings, E. W. Van Stryland, *J. Opt. Soc. Am. B* **1992**, 9, 2065.
- [40] M. H. Weiler, *Solid State Commun.* **1981**, 39, 937.
- [41] E. W. Van Stryland, M. A. Woodall, H. Vanherzeele, M. J. Soileau, *Opt. Lett.* **1985**, 10, 490.
- [42] I. M. Catalano, A. Cingolani, *Phys. Rev. B* **1979**, 19, 1049.
- [43] Y.-P. Chan, J.-H. Lin, C.-C. Hsu, W.-F. Hsieh, *Opt. Express* **2008**, 16, 19900.
- [44] J. Pan, M. I. B. Utama, Q. Zhang, X. Liu, B. Peng, L. M. Wong, T. C. Sum, S. Wang, Q. Xiong, *Adv. Mater.* **2012**, 24, 4151.
- [45] M. I. B. Utama, Q. Zhang, S. Jia, D. Li, J. Wang, Q. Xiong, *ACS Nano* **2012**, 6, 2281.
- [46] M. I. B. Utama, Z. Peng, R. Chen, B. Peng, X. Xu, Y. Dong, L. M. Wong, S. Wang, H. Sun, Q. Xiong, *Nano Lett.* **2010**, 11, 3051.
- [47] M. I. Bakti Utama, Q. Zhang, J. Zhang, Y. Yuan, F. J. Belarrie, J. Arbiol, Q. Xiong, *Nanoscale* **2013**, 5, 3570.
- [48] X. Liu, Q. Zhang, Q. Xiong, T. C. Sum, *Nano Lett.* **2013**, 13, 1080.

Title: Phonon-assisted Anti-Stokes Lasing in ZnTe Nanoribbons

Keywords: Zinc telluride; exciton-phonon coupling; anti-stokes emission; upconversion lasing; laser cooling;

TOC figure

Scheme 1. Electron Transition Schematics of Four types of up-converted photoluminescence.

(a) Excited states absorption (ESA) induced up-conversion emission. Two photons are absorbed via a real electronic state to excite a high energy carrier. (b) Energy transfer induced up-conversion (ETU). The energy of an excited carrier is transferred to a carrier on a real intermediate excited state to generate a carrier with higher energy. (c) Two-photon absorption (TPA) induced up-conversion. Two photons are absorbed one by one via a virtual electronic state to excite a high energy carrier. (d) Phonon-assisted anti-stokes photoluminescence (PA-ASPL). One phonon and several phonons are absorbed simultaneously to excite a carrier.

Figure 1. Stokes and anti-Stokes PL emission of individual ZnTe nanoribbons. (a) Scanning Electron microscopy image of as-grown ZnTe nanoribbons. (b-c) PL and Raman spectroscopy of individual ZnTe nanoribbon when excited by continuous-wave laser. The excitation wavelength is 532 nm (b) and 543 nm (c), which are also indicated by green arrows in the figures. The red curve and blue curve is taken at 220 K (273 K) and 120 K (215 K), respectively. At 220 K (273 K), the PL emission band is in the Stokes part of excitation laser. At 120 K (215 K), the PL emission band locates at the anti-Stokes part of excitation part. (d) Power-dependent ASPL emission intensity (red dots) and energy (black triangles) of the ZnTe nanoribbon. The sample temperature is 120 K and the excitation laser wavelength is 532 nm. Two functions are used to fit the power-dependent ASPL emission intensity curve. When the pumping intensity is smaller than $1200 \text{ W}/\text{cm}^2$, the emission intensity is linear to excitation power fluence (blue line); while when the pumping fluence is larger than is smaller than $1200 \text{ W}/\text{cm}^2$, the emission intensity is nearly linear to the square of excitation power (power law ~ 2.28 , green line). (e) Temperature-dependent ASPL emission spectroscopy of ZnTe nanoribbon. The excitation wavelength is 532 nm. The ASPL peak center is indicated by red arrow. The sample temperature is indicated near to each curve. (f) The intensity of Stokes-PL (blue dots) and anti-Stokes PL (red dots) as a function of temperature. Stokes-PL and anti-Stokes PL spectra are taken when the excitation wavelength is 473 nm and 532 nm.

Figure 2. Up-converted lasing emission of individual ZnTe nanoribbons. (a) White light illuminating optical (upper) and up-converted lasing image (lower) of individual nanoribbon. Excitation laser: 800 nm. (b)-(c) Up-converted lasing spectra of individual ZnTe nanoribbon. The excitation wavelength is: 800 nm (b); 550 nm (c). The inset figures show the lasing intensity dependent on excitation power. (d) Power dependent up-converted PL and lasing intensity when the ZnTe nanoribbon is excited by 800 nm, 680 nm, 600 nm, 550 nm and 545 nm.

Figure 3. Two photon absorption coefficient of ZnTe nanoribbons. (a) Normalized transmission intensity versus z position in z -scan measurement, where z is the distance beam from the incident laser focal point to sample. (b) Two photon absorbance (peak depth in 3a) as a function of excitation power (log-log scale). (c) The z -scan spectra when excitation wavelength is 550 nm, 580 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm. (d) Excitation wavelength dependent inverse of the two photon absorption coefficient constant α_2 (black dots) and up-conversion lasing threshold (red triangle).

Figure 4. (a) Upconversion spectra at different wavelength (indicated near to each spectrum). The cooling temperature is around 80 K. (b) Temperature of ZnTe nanoribbons as a function of excitation wavelength. The excited electron-hole pair density remains fixed around one third of lasing threshold. The temperature is evaluated using the emission wavelength extracted out from Fig. 4(a).

track change version

[Click here to download Supporting Information: manuscript with marked changes.doc](#)

Production Data

[Click here to download Production Data: Figure 1.tiff](#)

Production Data

[Click here to download Production Data: figure2.tiff](#)

Production Data

[Click here to download Production Data: Figure3.tiff](#)

Production Data

[Click here to download Production Data: Figure4.tiff](#)

Production Data

[Click here to download Production Data: Scheme 1.tiff](#)

Production Data

[Click here to download Production Data: TOC.tiff](#)