

View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Kim, C. Hwang, S. Y. Park, S. Ko, H. Park, W. C. Choi, J. B. Kim, D. S. Kim, S. Park, J. Y. Kim and H. Song, *J. Mater. Chem. A*, 2014, DOI: 10.1039/C4TA03358B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsA

Journal of Materials Chemistry A

RSCPublishing

PAPER

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50

High-yield synthesis of single-crystal silicon nanoparticles as anode materials of lithium ion batteries via photosensitizer-assisted laser pyrolysis[†]

Seongbeom Kim,[‡]^a Chihyun Hwang,[‡]^a Song Yi Park,^a Seo-Jin Ko,^a Hyungmin Park,^a Won Chul Choi,^b Jong Bok Kim,^c Dong Suk Kim,^d Soojin Park,^a Jin Young Kim^{a*} and Hyun-Kon Song^{a*}

Single crystal silicon nanoparticles (Si-NPs) of 20 nm were produced via a laser pyrolysis at a virtually complete conversion from SiH₄ into Si-NPs. SF₆ was used as the photosensitizer to transfer laser beam energy to silicon precursors, dramatically enhancing crystallinity of Si-NPs and their production efficiency. By using their well-developed crystalline structure, the directional volume expansion of Si-NPs was confirmed during lithiation. Lithiation/delithiation kinetics of our Si-NPs was superior to that of their amorphous counterparts due to the footprinted Li⁺ pathways formed during amorphization.

Introduction

Silicon nanoparticles (Si-NPs) have been broadening application boundaries of elemental silicon since they can be dispersed in various solvents via proper surface chemical treatments.^{1,2} Physicochemical properties inherited from bulk silicon as well as photoluminescence characteristics due to quantum confinement effects of Si-NPs facilitate their uses in optoelectronic devices, energy devices and biomedical imaging.³⁻¹⁶ As a practically foreseeable application, Si-NPs can be used as an anode material of Li-ion batteries (LIBs) with the highest gravimetric capacity (4200 mAhg⁻¹) among anode candidates developed until now. A number of attempts using nanostructured silicon for LIB applications have been made to overcome the demerits of silicon such as volume expansion, pulverization and evolving electrolyte decomposition which are practically observed with macro-sized silicon materials under repeated charge/discharge cycles.¹⁷⁻²⁰ Realizing full capacity of the silicon anodes with stable operations might shed light on ubiquitous environments and environment-friendly societies based on electric vehicles and smart grids.

Various methods are available for Si-NPs production. Si-NPs can be prepared from bulk silicon by using mechanical ball milling or chemical/electrochemical etching with distributed dimensions.^{21,22} By using plasma, Si-NPs are produced from gaseous precursors with high yield.²³ However, deposition of silicon is inevitable and large space is necessary for mass production system. Solution-phase synthesis of Si-NPs is also available but high temperature process is necessary.²⁴ Even if

Si-NPs have been introduced into market, the cost-effective production of Si-NPs is still emphasized. Compared with other laser pyrolysis of silicon precursor gases is methods, considered relatively more promising for production of Si-NPs in terms that *high-purity* Si-NPs can be produced without being exposed to contaminants in a continuous manner.^{22,23,25-29} High conversion efficiency of precursors to Si-NPs is practically important in the laser pyrolysis because of the high cost of the precursors. To save energy required for operating laser at high power, also, thermal loss should be reduced by directing the laser beam energy to the chemical conversion of precursors to Si-NPs in an efficient way. By using a photosensitizer, in this work, we successfully demonstrate a virtually complete conversion of silicon precursors (SiH₄) to Si-NPs by the laser pyrolysis. SF₆ as the photosensitizer absorb laser beam efficiently and release thermal energy that can be utilized for the conversion. We also demonstrate the stable operation of LIB using the Si-NPs as an anode material.

Experimental

Laser pyrolysis for Si-NPs synthesis

All the gas flows were controlled by mass flow controllers. CO_2 laser at 57 W (95% of maximum power) was used with the chamber pressure at 400 Torr. The produced Si-NPs were collected through a membrane filter installed in a tightly sealed collector. The Si-NPs were separated by a membrane filter and treated after being transferred to a N₂-filled glove box.

PAPER

Emission spectroscopy

Emission of reaction flames was measured through an optical fiber by a linear diode array (with a total length of 24.6 mm and a height of 3.0 mm) with a triple grating monochromator (focal length = 0.3 m, 1200 grooves/mm grating; SpectraPro-300i, Acton Research corporation). The spectra obtained were calibrated in wavelength (not intensity).

Cell preparation

Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50.

The Si-NPs were carbon-coated at 10 wt. % of the active material by vapor deposition. Toluene gases were introduced into a tube furnace at which the samples were located and carbonized at 900 °C for10 min. Coin-type half cells were configured with Si-NP-containing electrodes as a working electrode and lithium metal as a reference electrode. A separator (NH 716, Asahi) was sandwiched between the two electrodes. The working electrodes were prepared by coating mixture slurries on copper foils. The mixture slurries were made of the carbon coated Si-NPs with a mixed polysaccharide binder and carbon black at 60:20:20 in weight. Loading amount of the composite was 1.7 mg cm⁻² with 20 µm thickness.

Electrochemical tests

All the cells were galvanostatically lithiated and delithiated at indicated C-rates (WBCS3000S, WonATech). 1C was determined experimentally to be 1762 mA g^{-1} , based on the available capacity measured at low current discharge condition (0.05C based on the above definition).

Electrochemical impedance spectra were obtained from 200 kHz to 100 mHz (VMP3, BioLogic).

Results and Discussion

A CO₂ laser beam (10.6 μ m wavelength; continuous wave (CW)) crossed gas streams jetted from coaxially aligned inner and outer tubes (Fig. 1a). The feedstock gases containing SiH₄ with or without SF₆ and H₂ are supplied from the inner tube while helium gas is supplied by the outer tube to confine the gas stream lines. The main reaction to produce Si-NPs is:

$$SiH_4 \rightarrow Si + 2H_2$$
 (1)



Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50

The reference Si-NP sample have been prepared by the above simple reactions in absence of photosensitizers because SiH₄ molecules as a precursor is known to absorb the CO₂ laser beam at the 10.6 μ m wavelength.³⁰ In other cases such as Ge nanoparticle production, however, the use of photosensitizers is required because typical Ge-containing precursors (GeH₄) cannot absorb the laser beam efficiently.^{31,32} In this work, a photosensitizer (SF₆ here) was first used for Si-NP production to enhance the production yield, considering high absorption cross section of SF₆ molecules upon the CO₂ laser beam. The absorbed energy excites vibrational and rotational molecular motions of SF₆ and then is transferred to SiH₄ molecules via

Journal of Materials Chemistry A

dissociation and subsequent Si-NPs synthesis. The gas-to-solid conversion during the laser pyrolysis was calculated by the mass ratio of produced Si-NPs to SiH₄ gas passing through laser beam path (Fig. S1 to S5, the equation in Supplementary Information). By the help of SF₆, the gas-to-solid conversion increased significantly (Fig. 1b, Table S1). Without H₂ gas, the conversion increased more than six folds from 12.4 % to 75.0 % by addition of 5 standard cubic centimeters per minute (sccm) of SF₆. More amounts of SF₆ were not tested in absence of H₂ because uncontrollable detonation reactions with higher concentration of SF₆ was expected:

collisions³³ leading to an enhancement in SiH₄ molecule

$$3SiH_4 + 2SF_6 \rightarrow 2S + 3SiF_4 + 2HF + 5H_2$$
(2)

The detonation reaction during the photosensitizer-assisted laser pyrolysis might provoke fatal accidents as well as failures in Si-NPs production (Fig. S6).³⁴ Also, by-products of the detonation such as HF could make troubles to the facilities. To suppress the detonation reaction, 100 sccm of H₂ gas was additionally incorporated. The backward reaction of the eqn 2 is encouraged with the higher H2 concentration. Also, the reaction zone is maintained below the critical temperature of SF₆ dissociation by dilution with additional H₂. Surprisingly, the conversion increased up to 97.1 % in a condition of 10 sccm of SF₆ and 100 sccm of H₂. The small loss of Si-NPs is unavoidable due to the Si-NPs leftover on a membrane filter during weighing. Therefore, the most of SiH4 molecules is considered to convert to Si-NPs. Further increase of SF₆ flow rate up to 15 sccm in presence of the same contents of H₂ led to a dramatic decrease in conversion to 16.3 %. The detonation reaction was not controlled at the high concentration of SF_6 .

The competition between the silicon production reaction and the detonation reaction during the photosensitizer-assisted laser pyrolysis was investigated by emission spectra of reaction flames (Fig. 1c and d). Si-NPs emitted light in red to orange color (far left photo with SiH₄ in absence of the photosensitizer in Fig. 1c)³⁵ while flames from SiH₄-absent gas were in blue (far right photo with SF₆ in absence of the silicon precursor). Intensities of reaction flames increased significantly with SF₆ contents when compared with both the SF₆-absent and SiH₄-absent controls, indicating thermal activation of SF₆ and the

following energy transfer to SiH₄ or the detonation reactions between SF₆ and SiH₄. The colors of flames were blue-shifted with increasing concentration of SF₆ (Fig. 1d).³⁶ With 10 sccm SF₆ at which the virtually complete conversion was obtained, the emission spectrum was only intensified without spectral changes (or no color change) when compared with the SF₆absent but SiH₄-present control. It indicates the formation reaction of Si-NPs are dominant over the detonation reaction at the condition with producing more amount of Si-NPs. However, with 15 sccm and 60 sccm SF_6 , the detonation reaction would be competitively or dominantly involved. Blue spectral region became more emphasized so that the spectra at 60 sccm SF_6 finally reached the spectral shape similar to the SiH₄-absent but SF₆-present control (far right photo in Fig. 1c). One more characteristic of the spectra that should be notified is the periodic fluctuation of spectra only with the detonationdominant situations (15 to 60 sccm SF_6 in presence or absence of SiH₄). The periodic peaks observed in 350 to 450 nm and 850 to 950 nm are attributed to the emission from molecular vibration modes of HF as a product of the detonation reaction.^{34,37} Monitoring the spectra of the reaction flames makes it possible to distinguish detonation reaction from the Si-NPs production process.

(a) (b) $F_{6}: 0$ (b) $F_{6}: 0$ $F_{6}: 0$ $F_{6}: 0$ $F_{6}: 0$ $F_{6}: 0$ $F_{6}: 0$ $F_{6}: 10$ $F_{6}: 10$ $F_{6}: 10$

Fig. 2 a-d) HR-TEM images of Si-NPs produced with different contents of SF₆ in presence of SiH₄:25 sccm and H₂:100 sccm. Scale bar = 50 nm for (a), (c) and 10 nm for (b), (d). The flow rates of SF₆ were indicated as numbers in sccm.

Si-NPs of 15 to 20 nm in average (Fig. S7) were obtained successfully by the laser pyrolysis of SiH₄ (Fig. 2).The most distinguished feature between Si-NPs prepared in absence and presence of SF₆ (Si-NP(-SF₆) and Si-NP(+SF₆), respectively) is their crystallographic difference. Single crystalline Si-NPs were obtained in presence of SF₆ with their lattice fringes clear (Fig. Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50.

1.2

2c and d, Fig. S8) while polycrystalline Si-NPs were developed in absence of SF_6 (Fig. 2a and b). The lattice distance measured at 0.317 nm (Fig. 2d) matches with the spacing value of (111) plane of the silicon. The size distributions were fairly narrow for all samples: average size (standard deviation) = 18.6 nm (6 nm) for Si-NP(-SF₆) and 18.7 nm (4.3 nm) for Si-NP(+SF₆). Xray diffraction patterns and Raman spectra confirmed the higher crystallinity of the Si-NP(+SF₆) (Fig. 3) than that of the Si-NP(-SF₆). Crystallite size of the Si-NP($+SF_6$) was estimated at 20.1 nm by Scherer equation, which is approximates the particle sizes (Fig. 3a). Crystallinity of the Si-NP(+SF₆) was estimated more than five times as high as that of the Si-NP(-SF₆) in terms of the area fraction of crystalline phase in Raman spectra: 10 % for Si-NP(-SF₆) and 54 % for Si-NP(+SF₆) (Fig. 3b). Impurities such as sulfur or fluorine were not detected in the Si-NP(+SF₆) by energy dispersive spectrometer under the TEM (Fig. S9 and S10) while 0.4 wt. % sulfur was found in Si-NP(+SF₆) (Table S2). The higher crystallinity of Si-NPs which is produced by photosensitizer-assisted pyrolysis is due to the efficient absorption of energy from the laser beam by SF_6 and the following energy transfer to the conversion reaction to Si-NPs. The use of 10 sccm SF_6 would be an optimized condition in this work, achieving the virtually complete conversion from SiH₄ to Si-NPs while preventing detonation reactions. At this condition, the temperature of reaction zone would be controlled between ~900 K (dissociation temperature of SiH₄) and ~1500 K (dissociation temperature of SF_6)³⁸.



Fig. 3 (a) X-ray diffraction patterns of Si-NPs. (b) Raman spectra (Si-NP(-SF₆) at the top; Si-NP(+SF₆) at the bottom). The spectra were deconvoluted by using Gaussian and Lorentzian models for amorphous (~ 480 cm⁻¹) and crystalline (~ 520 cm⁻¹) phases. The area fractions of crystalline phase were estimated at 10 % for Si-NP(-SF₆) and at 54 % for Si-NP(+SF₆).

Electrochemical performances of alloying and dealloying of Si-NPs with lithium were investigated between Si-NP(-SF₆) and Si-NP(+SF₆) (Fig. S11). Both of them showed the same capacity retention during cycling charge and discharge at slow rates (0.2C and 0.5C, respectively) (Fig. 4a and b). Also, Si-NP(+SF₆) showed the rate-dependency of capacities similar to or a little bit superior to Si-NP(-SF₆) (Fig. 4c and d). More interestingly, however, the cyclability at fast charge and discharge rates revealed their intrinsic difference (Fig. 4e). The Si-NP(-SF₆) did not deliver electrochemically meaningful capacities at 3C for both lithiation and delithiation after the 600^{th} cycle. On the other hand, Si-NP(+SF₆) delivered its capacities at 36 % of the initial capacity at the 1000^{th} cycle.

1.2



Fig. 4 (a and b) Potential profiles and capacities (Q) during repeated cycles of lithiation at 0.2C and delithiation at 0.5C. (c and d) Potential profiles and capacities at various C-rates. Lithiation and delithiation rates were used at the same values as indicated. (e) Capacity retention with cycles at rates of 3C. (f and g) Electrochemical impedance spectra measured at 0.4 V after the 1st and 500th cycle. The possible reason for the capacity increase during the initial cycles (b) and after rate variation experiments (d) was discussed in Supplementary Information.

Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50

Journal of Materials Chemistry A

The electrochemically kinetic superiority of $Si-NP(+SF_6)$ to Si-NP(-SF₆) was supported by impedances (Fig. 4f and g). The single crystalline Si-NP(+SF₆) showed smaller resistance responsible for charge transfer through the interfaces between electrolyte and the solid-electrolyte interphase (SEI) layer (R_{SEI}) and/or between the SEI layer and silicon mass (R_{CT}), compared with their amorphous counterparts Si-NP(-SF₆). Due to serious merging between R_{SEI} and R_{CT} , the spectra were described by a single parallel circuit of resistance and capacitance: $R_{SEI+CT} = 14$ ohm for Si-NP(+SF₆) versus 37 ohm for Si-NP(-SF₆). After cycling, the semicircles responsible for charge transfer resistances were decoupled to two different ones as the SEI layer developed more. The higher-frequency parts (left ones) are related to R_{SEI} while the lower-frequency ones are for that of R_{CT}. Both of R_{SEI} and R_{CT} of Si-NP(+SF₆) were measured at still smaller values, compared with those of Si-NP(-SF₆): $R_{SEI} = 6$ ohm for Si-NP(+SF₆) versus 13 ohm for Si-NP(-SF₆); $R_{CT} = 10$ ohm for Si-NP(+SF₆) versus 25 ohm for Si- $NP(-SF_6)$.



Fig. 5 HR-TEM images of the amorphous Si-NP(-SF₆; a and c in the left column) and the single crystalline Si-NP(+SF₆; b and d in the right column) before (a and b in the first row) and after lithiation (c and d in the second row).

The next question would be why the single crystal Si-NP(+SF₆) showed better kinetics of lithiation/delithiation than their amorphous counterparts from the viewpoint of materials. Silicon experiences amorphization during dealloying process following the first alloying or lithiation.³⁹ There is no significant difference of crystallography between the single crystal Si-NP(+SF₆) and their amorphous or polycrystalline counterparts Si-NP(-SF₆) after the second cycle because both of them are amorphized. However, different morphologies were evolved after volume expansion caused by lithiation (Fig. 5). The amorphous Si-NP(-SF₆) experienced isotropic or non-directional dimensional changes, leaving hollow cores caused by outward growth of the silicon mass. On the contrary, the

single crystal Si-NP(+SF₆) showed anisotropic or directional volume expansion following a specific crystallographic direction. The preferential growth of volume expansion consists with an experimental evidence that the <110> direction of silicon is favored for the expansion because lithium ions preferentially diffuse along the channels.40 Also, a coarse structure was developed with the Si-NP(+SF₆) while a dense sphere was formed with Si-NP(-SF₆). We consider that the kinetic facility of the single crystal Si-NP(+SF₆) comes from a channel-footprinted morphology formed during amorphization. That is to say, the channels of lithium ions are memorized in the originally single-crystal Si-NPs during amorphization even if we cannot say there are aligned routes for lithium ions. A lithium diffusion pathway would follow a shortcut for alloying. In the synthetically-born amorphous $Si-NP(-SF_6)$, however, there would be less possibilities that the footprints are left because the Si-NPs were initially amorphous-phase-dominant. Lithium ions would travel via detours to find thermodynamically favored alloying sites. Therefore, the single-crystal Si-NPs are electrochemically advantageous over their amorphous counterparts due to in situ generation of Li⁺ diffusion channels during lithiation.

Conclusions

In summary, we presented a high-yield production of singlecrystal Si-NPs by using a photosensitizer-assisted laser pyrolysis. The unique point of this process is a third molecule (called photosensitizer), different from reactants and inert guiding gases, transfers energy of the laser beam to the silicon precursors in a more efficient way. Use of SF₆ as the photosensitizer enhanced the production yield up to virtually complete conversion from SiH₄ to Si-NPs (97.1%) and degree of Si-NP's crystallinity. We could investigate the directional volume expansion of Si-NPs in a clear manner after lithiation because our particles had well-defined crystallographic planes developed throughout a whole particle dimension. We believe this work would provide an impact to industrial as well as academic societies in terms of enabling *mass production* of *single-crystal* nanoparticles.

Acknowledgements

This work was supported by MOTIE (Star : 20135020900030), KETEP (2012T100100740), MOE (BK21Plus : META, 10Z20130011057) and KIER (B4-2424), Korea.

Notes

^{*a*} Department of Energy Engineering and School of Energy and Chemical Engineering, UNIST, Ulsan 698-798, (Korea) E-mail: philiphobi@hotmail.com, jykim@unist.ac.kr

^b Korea Institute of Machinery and Materials (KIMM), Yuseong-gu, Daejeon 305-343, (Korea)

^c School of Advanced Materials and System Engineering, Kumho National Institute of Technology, Gumi 730-701 (Korea)

^d KIER-UNIST Advanced Center for Energy, Korea Institute of Energy Research, Ulsan 689-798, (Korea)

[†] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

\$Seongbeom Kim and Chihyun Hwang contributed equally to this work.

References

Published on 02 September 2014. Downloaded by Michigan Technological University on 11/09/2014 02:36:50

- F. Hua, M. T. Swihart, E. Ruckenstein, *Langmuir* 2005, 21, 6054-6062.
- 2 L. M. Wheeler, N. R. Neale, T. Chen, U. R. Kortshagen, *Nat. Commun.* 2013, **4**, 2197.
- 3 U. Gösele, Nat. Nanotechnol. 2008, 3, 134-135.
- 4 W. D. A. M. de Boer, D. Timmerman, K. Dohnalova, I. N. Yassievich, H. Zhang, W. J. Buma, T. Gregorkiewicz, *Nat. Nanotechnol.* 2010, 5, 878-884.
- 5 M. Stupca, M. Alsalhi, T. Al Saud, A. Almuhanna, M. H. Nayfeh, *Appl. Phys. Lett.* 2007, **91**, 063107.
- 6 C.-Y. Liu, Z. C. Holman, U. R. Kortshagen, *Nano Lett.* 2008, 9, 449-452.
- 7 Z. C. Holman, C.-Y. Liu, U. R. Kortshagen, *Nano Lett.* 2010, 10, 2661-2666.
- 8 K.-Y. Cheng, R. Anthony, U. R. Kortshagen, R. J. Holmes, *Nano Lett.* 2011, **11**, 1952-1956.
- 9 S. Kim, K. Jeon, J. C. Lee, M. T. Swihart, M. Yang, Appl. Phys. Express 2012, 5, 2302.
- 10 S. Kim, J. H. Lee, M. T. Swihart, J.-C. Lee, J. Y. Kim, *Curr. Appl. Phys.* 2014, 14, 127-131.
- 11 F. Erogbogbo, T. Lin, P. M. Tucciarone, K. M. LaJoie, L. Lai, G. D. Patki, P. N. Prasad, M. T. Swihart, *Nano Lett.* 2013, 13, 451-456.
- 12 J.-H. Park, L. Gu, G. von Maltzahn, E. Ruoslahti, S. N. Bhatia, M. J. Sailor, *Nat. Mater.* 2009, 8, 331-336.
- 13 C. M. Hessel, M. R. Rasch, J. L. Hueso, B. W. Goodfellow, V. A. Akhavan, P. Puvanakrishnan, J. W. Tunnel, B. A. Korgel, *Small* 2010, 6, 2026-2034.
- 14 F. Erogbogbo, C.-W. Chang, J. L. May, L. Liu, R. Kumar, W.-C. Law, H. Ding, K. T. Yong, I. Roy, M. Sheshadri, M. T. Swihart, P. N. Prasad, *Nanoscale* 2012, 4, 5483-5489.
- 15 J. Liu, F. Erogbogbo, K. T. Yong, L. Ye, J. Liu, R. Hu, H. Chen, Y. Hu, Y. Yang, J. Yang, I. Roy, N. A. Karker, M. T. Swihart, P. N. Prasad, ACS Nano 2013, 7, 7303-7310.
- 16 S. Bhattacharjee, I. M. Rietjens, M. P. Singh, T. M. Atkins, T. K. Purkait, Z. Xu, S. Regli, A. Shukaliak, R. J. Clark, B. S. Mitchell, G. M. Alink, A. T. M. Marcelis, M. J. Fink, J. G. C. Veinot, S. M. Kauzlarich, H. Zuilhof, *Nanoscale* 2013, 5, 4870-4883.
- 17 C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* 2008, **3**, 31-35.
- 18 B. Hertzberg, A. Alexeev, G. Yushin, J. Am. Chem. Soc. 2010, 132, 8548-8549.
- 19 L.-F. Cui, L. Hu, H. Wu, J. W. Choi, Y. Cui, J. Electrochem. Soc. 2011, 158, A592-A596.
- 20 H. Wu, Y. Cui, Nano Today 2012, 7, 414-429.
- 21 C. Diaz-Guerra, A. Montone, J. Piqueras, F. Cardellini, Semicond. Sci. Technol. 2002, 17, 77-82.

- 22 L. T. Canham, Appl. Phys. Lett. 1990, 57, 1046-1048.
- 23 L. Mangolini, E. Thimsen, U. Kortshagen, Nano Lett. 2005, 5, 655-659.
- 24 C. M. Hessel, D. Reid, M. G. Panthani, M. R. Rasch, B. W. Goodfellow, J. W. Wei, H. Fujii, V. Akhavan, B. A. Korgel, *Chem. Mater.* 2012, 24, 393-401.
- 25 C. M. Hessel, D. Reid, M. G. Panthani, M. R. Rasch, B. W. Goodfellow, J. Wei, H. Fujii, V. Akhavan, B. A. Korgel, *Chem. Mater.* 2011, 24, 393-401.
- 26 W. R. Cannon, S. C. Danforth, J. H. Flint, J. S. Haggerty, R. A. Marra, J. Am. Ceram. Soc. 1982, 65, 324-330.
- 27 M. Ehbrecht, B. Kohn, F. Huisken, M. A. Laguna, V. Paillard, *Phys. Rev. B* 1997, 56, 6958.
- 28 G. Ledoux, J. Gong, F. Huisken, O. Guillois, C. Reynaud, Appl. Phys. Lett. 2002, 80, 4834-4836.
- 29 O. Sublemontier, H. Kintz, F. Lacour, X. Paquez, V. Maurice, Y. Leconte, D. Porterat, N. Herlin-Boime, C. Reynaud, *Kona* 2011, 29, 2011.
- 30 W. Steward, H. Nielsen, Phys. Rev. 1935, 47, 828-832.
- 31 W. Steward, H. Nielsen, Phys. Rev. 1935, 48, 861-864.
- 32 S. Kim, B. Walker, S. Y. Park, H. Choi, S. –J. Ko, J. Jeong, M. H. Yun, J. C. Lee, D. S. Kim, J. Y. Kim, *Nanoscale* 2014, 6, 10156-10160.
- 33 J. W. I. Vanbladel, A. Vanderavoird, J. Chem. Phys. 1990, 92, 2837-2847.
- 34 S. H. Bauer, J. A. Haberman, *IEEE Journal of Quantum Electronics* 1978, 14, 233-237.
- 35 R. A. Bauer, J. G. M. Becht, F. E. Kruis, B. Scarlett, J. Schoonman, J. Am. Ceram. Soc. 1991, 74, 2759-2768.
- 36 J. W. I. van Bladel, A. van der Avoird, J. Chem. Phys. 1990, 92, 2837-2847.
- 37 K. von Puttkamer, M. Quack, Chem. Phys. 1989, 139, 31-53.
- 38 W. Fu, T. P. Cotter, Appl. Phys. 1977, 12, 265-276.
- 39 C. M. Park, J. H. Kim, H. Kim, H. J. Sohn, *Chem. Soc. Rev.* 2010, **39**, 3115-3141.
- 40 S. W. Lee, M. T. McDowell, J. W. Choi, Y. Cui, *Nano Lett.* 2011, 11, 3034-3039