Thermo-optical response of photonic crystal cavities operating in the visible spectral range

Janik Wolters¹, Niko Nikolay¹, Max Schoengen², Andreas W Schell¹, Jürgen Probst², Bernd Löchel² and Oliver Benson¹

¹ Nano-Optics, Institute of Physics, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany
² Institute for Nanometre Optics and Technology, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Straße 15, D-12489 Berlin, Germany

E-mail: janik.wolters@physik.hu-berlin.de

Received 25 February 2013, in final form 11 June 2013
Published 15 July 2013
Online at stacks.iop.org/Nano/24/315204

Abstract
In this paper we study thermo-optical effects in gallium phosphite photonic crystal cavities in the visible range. By measuring the shift of narrow resonances, we derive the temperature dependency of the local refractive index of gallium phosphide in an attoliter volume over a temperature range between 5 and 300 K at a wavelength of about 605 nm. Additionally, the potential of photonic crystal cavities for thermo-optical switching of visible light is investigated. As an example we demonstrate thermo-optical switching with 13 dB contrast.

(Some figures may appear in colour only in the online journal)

1. Introduction
Photonic crystal (PC) nanocavities have increasing importance for quantum optics, photonics and sensing applications [1]. The main reason for this is their ability to confine the electromagnetic field in a volume comparable to the cubic wavelength and thus to strongly enhance light–matter interaction [2, 3]. Using PC cavities, not only has the Purcell enhancement of single quantum emitters been shown [4–6] but the strong coupling regime of cavity quantum electrodynamics has also been reached with single quantum dots in PC cavities [7–9]. With such systems, lasing oscillations of a single quantum dot [10] and ultrafast all-optical switching by sub-femtojoule pulses [11] and single photons have been demonstrated [12].

The high quality factor of PC cavities corresponds to a narrow resonance line. Its shift is a very sensitive indicator for local modifications of the optical properties. A prominent example of such modifications is the dependency of the refractive index on the local temperature. Cooling of PC cavities is mandatory for many quantum optics experiments, since emission rate and coherence of most quantum emitters improve drastically [13]. However, for complex integrated circuits [3, 7, 15] operating at cryogenic temperatures as intended, the shifts of the resonance wavelength and modifications of quality factors [14] of individual elements have to be compensated. Therefore, design and material properties should be known a priori. In this paper we first investigate in detail the resonance shift of a PC cavity from room temperature to 5 K. From this we derive the index of refraction of the cavity material (GaP) as a basis for a predictable design of PC structures in the visible spectral range.

In a second part of the paper, local heating and its effect on the PC cavity resonances is investigated. We perform experimental studies of thermo-optical switching of visible light. Based on theoretical analysis we estimate that due to the ultra-small volume of PC cavities even thermal effects may occur with very short time constants.

2. Photonic crystals in gallium phosphide
The PC structures used throughout our experiments are made of GaP and operate in the visible from 600 to 650 nm [18, 4].
In this material thermal expansion can be neglected and the only relevant process when changing the temperature is the change of the refractive index $n$ [16, 17]. This effect is exploited throughout our experiments.

First, we designed 55 nm thick free-standing PC slabs (lattice constant 209 nm) with so-called L3 cavities [2] using three-dimensional finite time domain (FDTD) simulations (Lumerical). These cavities are formed by three missing holes in a trigonal lattice. They support several spectrally narrow modes of high quality factors [19]. The electromagnetic field of the fundamental mode is concentrated mainly within GaP on about seven unit cells, corresponding to a material volume of 14 attoliter (al) (see figure 1). The emission profile of this fundamental cavity mode is polarized perpendicular to the cavity axis [20], a feature that we will use later on to measure the thickness of the slab or on the hole diameter in the studied regime.

For example, changing the refractive index of the PC membrane by about 100 ppm corresponds to a wavelength shift by $(54 \pm 1)$ pm, which can be detected by a spectrograph and is relevant for experiments with high-$Q$ cavities [7]. FDTD simulations show that in the studied regime the change of the resonance with the refractive index does not depend on the thickness of the PC slab (figure 2). Thus, a change in the resonance wavelength is a very precise measure for changes in the refractive index, even if the exact geometry is not known. In contrast to other methods allowing refractive index measurements in bulk material [25] or thin membranes [26], this allows measurements in ultra-small volumes of the order of 10 al. To the best of our knowledge this is the smallest volume in which refractive index measurements have ever been performed.

We fabricated the structures by electron beam lithography (EBL) using a Vistec 5000+ electron beam lithography system with an acceleration voltage of 100 kV. In this way a 59 nm heteroepitaxial gallium phosphide (GaP) layer was deposited on a silicon (100) substrate [21–23]. The lithography step was done in a 2.2 M PMMA resist layer spincoated on the GaP layer and exposed by EBL at a dose of 700 $\mu$C cm$^{-2}$. The designed structure was transferred to the GaP layer by dry-etching with boron trichloride (BCl$_3$) and a subsequent removal of the underlying Si layer by isotropic dry-etching with sulfur hexafluoride (SF$_6$). After the fabrication process the whole sample was cleaned in an oxygen plasma using an Oxford Plasmalab 80. We estimate that the final PC membrane has a thickness of 55 nm. Importantly, due to a tiny lattice mismatch, the GaP layer is strained and may bend when it is under-etched. To allow for expansion without bending, we designed spring-like membrane supports (see figure 7(a)).

After processing, the quality and geometric precision of the structures were measured using scanning electron and atomic force microscopy (AFM). Figure 1(b) shows an AFM image of the fabricated structure.

3. Refractive index measurement

3.1. Experimental methods

To control the cavity temperature within a wide range, the sample was mounted on the cold finger of a continuous flow He-cryostat. By changing the He-flow and additional heating, the temperature could be precisely regulated in the range between 5 and 300 K. In parallel, the spectral position of the cavity resonance was measured. Usually, the intrinsic material fluorescence under incoherent excitation is analyzed with a spectrograph for this purpose [24]. Here, this method could not be applied, as the excitation of fluorescence requires relatively strong lasers (in the order of 10 $\mu$W), which would unavoidably heat the PC cavity. To avoid this heating, we analyzed the reflected light in the crossed polarization scheme [27]. In this scheme only very low illumination power is needed ($P < 100$ nW). By doubling the power and comparing the position of the cavity resonance we could guarantee that the radiation has negligible influence on the cavity temperature ($<1$ K).

In detail, the cavity is illuminated with a vertical polarized collimated white light beam from a supercontinuum source (NKT Photonics SuperK) focused on the cavity by a microscope objective with a numerical aperture of 0.9
A sketch of the optical setup to measure the cavity resonance in the cross polarized detection scheme. The sample with the PC cavities is placed in the vacuum of a continuous flow He-cryostat to regulate the temperature. The PC cavity is illuminated with vertical polarized white light (≈100 nW) from a supercontinuum source through an objective lens with high numerical aperture. The horizontal polarized component of the reflected light is detected in a confocal scheme by a spectrograph. The cavity axis is rotated by 45° with respect to the polarization basis. Thus, the polarization of the reflected light is slightly rotated at the cavity resonance. See text for details.

(Resputo), which is placed inside the insulation vacuum of the cryostat. Importantly, the axis of the cavity is rotated by 45° with respect to the incident polarization. The reflected light is collected through the same objective lens, but only the horizontal polarized component of the reflected light is detected with a 500 mm spectrometer (Acton SpectraPro 500i) from a supercontinuum source through an objective lens with high numerical aperture. The horizontal polarized component of the reflected light is detected in a confocal scheme by a spectrograph. The cavity axis is rotated by 45° with respect to the polarization basis. Thus, the polarization of the reflected light is slightly rotated at the cavity resonance. See text for details.

The cavity axis is rotated by 45° with respect to the polarization direction. The reflected light is collected through the same objective lens, but only the horizontal polarized component of the reflected light is detected with a 500 mm spectrometer (Acton SpectraPro 500i) from a supercontinuum source through an objective lens with high numerical aperture. The horizontal polarized component of the reflected light is detected in a confocal scheme by a spectrograph. The cavity axis is rotated by 45° with respect to the polarization basis. Thus, the polarization of the reflected light is slightly rotated at the cavity resonance. See text for details.

3.2. Temperature dependency of the refractive index of GaP and the cavity resonance

In the following, the resonance wavelength of the fundamental mode of a cavity with hole radius $r = 63$ nm fabricated on the same sample was measured at various temperatures between 5 K and near room temperature. To verify the reproducibility, the data were taken in two subsequent cooling and heating cycles. We calculated the refractive index $n$ from the change of the resonance wavelength according to the relation

$$n(T) = n_{300 \text{K}} + [\lambda(T) - \lambda_{300 \text{K}}] a_{55},$$  

with the refractive index at room temperature $n_{300 \text{K}} = 3.34537$ from [29], the measured resonance wavelength at room temperature $\lambda_{300 \text{K}} = (608.20 \pm 0.01) \text{ nm}$ and the slope $a_{55} = 1/(163.36 \pm 0.01) \text{ nm}$ gained from the FDTD simulations for a slab thickness $t$ of 55 nm (figure 2). The resulting data and fitted curves are shown in figure 5. Above 100 K the refractive index changes linearly according to

$$n(T) = 3.290 \pm 0.001 + (180 \pm 20) \times 10^{-6} T \text{ K}^{-1}.$$  

This is in very good agreement with values for the refractive index of GaP at temperatures above 100 K, as reported in [16]. Interestingly, the slope decreases at a temperature of $T \approx 100$ K and the refractive index follows

$$n(T) = 3.302 \pm 0.001 + (67 \pm 7) \times 10^{-6} T \text{ K}^{-1}.$$  

We tried to fit the entire dataset shown in figure 5 with an exponential function, but the two-slope model represented by

Figure 3. A sketch of the optical setup to measure the cavity resonance in the cross polarized detection scheme. The sample with the PC cavities is placed in the vacuum of a continuous flow He-cryostat to regulate the temperature. The PC cavity is illuminated with vertical polarized white light (≈100 nW) from a supercontinuum source through an objective lens with high numerical aperture. The horizontal polarized component of the reflected light is detected in a confocal scheme by a spectrograph. The cavity axis is rotated by 45° with respect to the polarization basis. Thus, the polarization of the reflected light is slightly rotated at the cavity resonance. See text for details.

Figure 4. Exemplary spectrum and the corresponding fit with three Fano resonances at (637.03 ± 0.01), (630.59 ± 0.01) and (627.68 ± 0.01) nm to illustrate the measurement method. The spectrum was measured on an L3 cavity with hole radius $r = 50$ nm at a temperature of 300 K.
equations (3) and (4) is clearly more accurate. Although to the best of our knowledge no low temperature data for the optical refractive index are available in the literature, the kink at about 100 K is qualitatively in agreement with [30].

3.3. Influence of temperature on the quality factor

According to FDTD simulations the $Q$-factor of $Q \approx 2500$ is almost unaffected by a small change of the refractive index. We find experimentally that the decrease of the refractive index is followed by an increasing $Q$-factor (figure 6). Starting with a value of $560 \pm 50$ at room temperature, the $Q$-factor of the fundamental mode increases linearly with decreasing temperature. The highest measured $Q$-factor of $1150 \pm 50$ is more than twice the initial value at room temperature. We attribute this behavior to reduced material absorption [31, 32] at low temperature due to freeze-out of phonons. This dependency highlights the importance of considering not only the desired operation wavelength, mode volume and $Q$-factor, but also the operation temperature of PC cavities.

4. Thermo-optical switching

The shift of the PC cavity resonance as a function of temperature can also be used to implement integrated thermo-optical switching. Such switches have been demonstrated in the infrared. There, a modification of the refractive index via optical free carrier injection [33–35] is preferable due to the faster switching speed needed in telecom technology. In the following, we exploit switching in the visible spectral range. Since the size of integrated optical devices scales with the third power of the wavelength, cavity-based switching can be achieved with much smaller cavity volumes. As we will show, in principle this leads to fast switching speeds even via thermo-optical effects.

4.1. Theoretical predictions

To estimate the energy required to switch the device, we assume a specific heat of 410 J (kg K)$^{-1}$ [37, 38] at an operation temperature of 250 K. Assuming that the cavity volume is heated by a short laser pulse and using our experimental findings from section 4, we find that the cavity resonance shift directly after the laser pulse is 1.3 pm $fJ^{-1}$ of deposited energy. For cavities with moderate $Q$-factors of 10 000 the temperature induced resonance shift is of the order of the width of the resonance, when depositing 48 fJ. Thus thermo-optical switching with less than 50 fJ switching energy is feasible. To further reduce the energy required for switching, the operation temperature might be further reduced.

Thermal radiation in the device can be neglected and the dynamic behavior of the temperature $T$ is governed by the heat equation

$$\frac{\partial}{\partial t}T(x, t) = \alpha(x) \Delta T(x, t)$$

where the thermal diffusivity $\alpha(x)$ at position $x$ equals the diffusivity in GaP $\alpha_{\text{GaP}} = k/\rho c_p = 66 \times 10^{-3}$ $\mu$m$^2$ ns$^{-1}$ [39] in the membrane, while it is zero in the holes. To investigate the switching dynamics, we performed two-dimensional finite-difference simulations of the heat transport within the PC membrane and the mechanical support. The problem was tackled in detail using the Crank–Nicolson method [40] and the remaining sparse system was solved by the conjugate gradient method [41]. Here, Dirichlet boundaries were used to implement the heat reservoir of the bulk material, whereas Neumann boundaries were used to simulate the PC holes which inhibit the heat conduction process. Figure 7(a) shows the resulting temperature distribution in the PC slab at different times after the injection of a 3.7 pJ heat pulse. It can clearly be seen that in the case of a single pulse the comparable small thermal conductivity of the membrane holders has no effect. To estimate the switching speed, the
temperature evolution at the cavity position was evaluated (figure 7(b)). This temperature evolution can be perfectly fitted with the analytical solution of the heat equation for a two-dimensional slab

\[ T(t) = \frac{1}{4\pi \alpha_{\text{eff}}(t-t_0)}, \]

where the effective diffusion coefficient \( \alpha_{\text{eff}} = (42.61 \pm 0.04) \times 10^{-3} \, \mu \text{m}^2 \, \text{ns}^{-1} \). Remarkably, this cannot be explained by an average diffusivity deduced from the PC filling factor \( \beta = 0.8 \), which is \( \beta \alpha_{\text{GaP}} = 53 \times 10^{-3} \, \mu \text{m}^2 \, \text{ns}^{-1} \). Furthermore, according to equation (6) the cavity temperature difference is decreased to \( 1/e \) of the initial value after the time \( \tau = 1.2 \, \text{ns} \). Thus, the device promises switching speeds in the order of 1 ns. In contrast for longer pulses, where the dynamics is limited by the heat transport through the support springs we find \( \tau \approx 680 \, \text{ns} \). To increase the switching speed, the structure might be partially covered with a thin gold layer to increase the thermal conductivity and thereby allow for faster switching. Furthermore the operation temperature might be further decreased, resulting in an improved ratio between specific heat and diffusivity.

**4.2. Experimental implementation**

To experimentally verify our simulations, we pumped the PC cavity material with a switchable blue 405 nm laser (PicoQuant LDH-P-C-405B). The light is efficiently absorbed thus heating the cavity. Simultaneously, while switching the heating laser, we probed the cavity resonance as described in section 3.1. We used the spectrometer as a monochromator and detected the light at the cavity wavelength with a fast avalanche photodiode. This allowed for a high time resolution of up to 1 ns.

The observable contrast when switching the heating laser on and off exceeded 13 dB. Nevertheless, we could only observe switching times in the order of about 1 ms (figure 8) for laser powers of about 73 \( \mu \text{W} \). This is over three orders of magnitude slower than predicted. Furthermore, the required heating power is several orders of magnitude above the predicted value. The large deviation originates in the parasitic heating of the entire substrates; a major fraction of the heating laser is absorbed in the silicon substrate, rather than in the membrane. Thus the whole sample is heated up, which requires more energy and is much slower. Using transparent substrates or a different heating mechanism, these problems might be solved in future experiments. Nevertheless, the current configuration is already suitable to perform active control of the membrane temperature [7].

**5. Conclusion**

In conclusion, we demonstrated how the narrow resonance of a GaP PC cavity shifts due to cooling. From these data we precisely calculated the refractive index of GaP in the ultra-small cavity volume over the whole temperature range from near room temperature to \( T = 5 \, \text{K} \). This knowledge is crucial for the design and testing of PC structures and might also be used for novel PC applications. For example, the presented method may be used to determine the exact local
cavity temperature. This is of great importance if quantum emitters are coupled to the cavity, as the emission properties of such emitters strongly change with the temperature. In most previous experiments the temperature of the cold finger of the cryostat was given as a temperature reference. However, the cavity structure may be weakly thermally coupled to the cold finger and excitation light may locally heat the cavity. This is particularly an issue when studying under-etched PC membrane cavities and diamond defect centers as emitters, which require a relatively large excitation power \[4, 36\].

Finally, the refractive index can be measured using our method for any material where fabrication of a resonant photonic structure is possible.

In the second part of the paper we investigated GaP PC cavities for thermo-optical switching applications. By numerical simulations, we found switching speeds of up to 1 ns and outlined strategies to further improve this value. Furthermore, we realized a thermo-optical switch with 13 dB contrast between the on- and off-states.

Acknowledgments

This work was supported by the DFG (BE2224/9). J Wolters acknowledges funding by the state of Berlin (Elsa-Neumann). We thank H Dösch and T Hannappel for providing GaP on Si wafers. We thank PicoQuant GmbH for collaboration and support.

References

[1] Vahala K J 2003 Optical microcavities Nature \textbf{424} 839–46
[2] Akahane Y, Asano T, Song B S and Noda S 2003 High-$Q$ photonic nanocavity in a two-dimensional photonic crystal Nature \textbf{425} 4–7
[3] O’Brien J L, Furusawa A and Vuckovic J 2009 Photonic quantum technologies Nature Photon. \textbf{3} 687–95
[4] Wolters J, Schell A W, Kews G, Nüsse N, Schoengen M, Döschner H, Hannappel T, Löchel B, Barth M and Benson O 2010 Enhancement of the zero phonon line emission from a single nitrogen vacancy center in a nanodiamond via coupling to a photonic crystal cavity Appl. Phys. Lett. \textbf{97} 141108
[5] Englund D, Shields B, Rivoire K, Hatami F, Vuckovic J, Park H and Lukin M D 2010 Deterministic coupling of a single nitrogen vacancy center to a photonic crystal cavity Nano Lett. \textbf{10} 3922–6
[6] Englund D, Faraon A, Zhang B, Yamamoto Y and Vuckovic J 2007 Generation and transfer of single photons on a photonic crystal chip Opt. Express \textbf{15} 5550–8
[7] Englund D, Faraon A, Fushman I, Stoltz N, Petroff P and Vuckovic J 2007 Controlling cavity reflectivity with a single quantum dot Nature \textbf{450} 857–61
[8] Faraon A, Majumdar A, Englund D, Kim E, Bajcsy M and Vuckovic J 2011 Integrated quantum optical networks based on quantum dots and photonic crystals New J. Phys. \textbf{13} 055025
[9] Yoshih T, Scherer A, Hendrickson J, Khitrova G, Gibbs H M, Rupper G, Ell C, Shchekin O B and Deppe D G 2004 Vacuum Rabi splitting with a single quantum dot in a photonic crystal nanocavity Nature \textbf{432} 9–12
[10] Nomura M, Kumagai N, Iwamoto S, Ota Y and Arakawa Y 2010 Laser oscillation in a strongly coupled single-quantum-dot-nanocavity system Nature Phys. \textbf{6} 279–83
[11] Nozaki K, Tanabe T, Shinya A, Matsuo S, Sato T, Taniyama H and Notomi M 2010 Sub-femtojoule all-optical switching using a photonic-crystal nanocavity Nature Photon. \textbf{4} 477–83
[12] Volz T, Reinhard A, Winger M, Hennessy K J and Hu E L 2012 Ultrafast all-optical switching by single photons Nature Photon. \textbf{6} 605–9
[13] Henneberger F and Benson O 2009 Semiconductor Quantum Bits (Singapore: Pan Stanford Publishing)
[14] Joannopoulos J D, Johnson S G, Winn J N and Meade R D 2008 \textit{Molding the Flow of Light} (Princeton, NJ: Princeton University Press)
[15] Benson O 2011 Assembly of hybrid photonic architectures from nanophotonic constituents Nature \textbf{480} 193–9
[16] Piskin A N, Prokopenko V T, Rondarev V S and Yas’kov A D 1977 Refraction of light in gallium phosphide J. Appl. Spectrosc. \textbf{27} 1047–52
[17] Slack G A and Bartram S F 1975 Thermal expansion of some diamondlike crystals J. Appl. Phys. \textbf{46} 89
[18] Rivoire K, Faraon A and Vuckovic J 2008 Gallium phosphide photonic crystal nanocavities in the visible Appl. Phys. Lett. \textbf{93} 063103
[19] Chalcraft R et al 2007 Mode structure of the L3 photonic crystal cavity Appl. Phys. Lett. \textbf{90} 241117
[20] Barth M, Stingl J and Benson O 2008 Emission properties of high-$Q$ silicon nitride photonic crystal heterostructures Appl. Phys. Lett. \textbf{93} 021112
[21] Döschner H, Hannappel T, Kunert B, Beyer A, Volz K and Stolz W 2008 In situ verification of single-domain III–V on Si(100) growth via metal–organic vapor phase epitaxy Appl. Phys. Lett. \textbf{93} 172110
[22] Döschner H and Hannappel T 2010 \textit{In situ} reflection anisotropy spectroscopy analysis of heteroepitaxial GaP films grown on Si(100) J. Appl. Phys. \textbf{107} 123523
[23] Döschner H, Supplie O, Brückner S, Hannappel T, Beyer A, Ohlmann J and Volz K 2011 \textit{In situ} characterization of Si(100) substrates at the initial stage of III–V heteroepitaxy J. Cryst. Growth \textbf{315} 16–21
[24] Barth M, Koubu J, Stingl J, Löchel B and Benson O 2007 Modification of visible spontaneous emission with silicon nitride photonic crystal nanocavities Opt. Express \textbf{15} 17231–40
[25] Bertolotti M, Bogdanov V, Ferrari A, Jascow A, Nazorova N, Piskin A and Schirone L 1990 Temperature dependence of the refractive index in semiconductors \textit{J. Opt. Soc. Am. B} \textbf{7} 918
[26] Coccorullo G, Della Corte F G, Moretti L, Rendina I and Rubino A 2002 Measurement of the thermo-optic coefficient of a-Si:H at the wavelength of 1500 nm from room temperature to 200 °C \textit{J. Non-Cryst. Solids} \textbf{299} 310
[27] Galli M, Portalupi S L, Belotti M, Andreani L C, O’Faoilain L and Krauss T F 2009 Light scattering and Fano resonances in high-$Q$ photonic crystal nanocavities Appl. Phys. Lett. \textbf{94} 071101
[28] Fano U 1961 Effects of configuration interaction on intensities and phase shifts Phys. Rev. \textbf{124} 1866–78
[29] 2002 \textit{Landolt-Börnstein} \textit{41A1b: Group IV Elements, IV–IV and III–V Compounds. Part b—Electronic, Transport, Optical and Other Properties} (Berlin: Springer)
[30] Samara G 1983 Temperature and pressure dependences of the dielectric constants of semiconductors Phys. Rev. B \textbf{27} 3494–505
[31] Dean P and Thomas D 1966 Intrinsic absorption-edge spectrum of gallium phosphate Phys. Rev. \textbf{150} 690–703
[32] Subashiev V K and Chalikyan G A 1966 The absorption spectrum of gallium phosphate between 2 and 3 eV Phys. Status Solidi b \textbf{13} K91
[33] Belotti M et al 2008 All-optical switching in 2D silicon photonic crystals with low loss waveguides and optical cavities Opt. Express \textbf{16} 11624–36
[34] Hu X, Jiang P, Ding C, Yang H and Gong Q 2008 Picosecond and low-power all-optical switching based on an organic photonic-bandgap microcavity Nature Photon. 2 185–9

[35] Tanabe T, Notomi M, Mitsugi S, Shinya A and Kuramochi E-2005 All-optical switches on a silicon chip realized using photonic crystal nanocavities Appl. Phys. Lett. 87 151112

[36] Wolters J et al 2012 Coupling of single nitrogen vacancy defect centers in diamond nanocrystals to optical antennas and photonic crystal cavities Phys. Status Solidi b 249 918–24

[37] Merrill L 1977 Behavior of the AB-type compounds at high pressures and high temperatures J. Phys. Chem. Ref. Data 6 1205

[38] Tmar M, Gabriel A, Chatillon C and Ansara I 1984 Critical analysis and optimization of the thermodynamic properties and phase diagrams in the III–V compounds: the In-P and Ga-P systems J. Cryst. Growth 68 557

[39] Weil R and Groves W O 1968 The elastic constants of gallium phosphide J. Appl. Phys. 39 4049

[40] Crank J and Nicolson P 1947 A practical method for numerical evaluation of solutions of partial differential equations of the heat conduction type Math. Proc. Camb. Phil. Soc. 43 50

[41] Hestenes M R and Stiefel E 1952 Methods of conjugate gradients for solving linear systems J. Res. Natl Bur. Stand. 49 409