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Thermodynamic Processes on a Semiconductor Surface during *In-Situ* Multi-Beam Laser Interference Patterning

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Abstract: Laser interference has been widely used to produce one-dimensional gratings and more recently has shown great potential for two-dimensional patterning. In this paper, we examine by simulation, its application to *in-situ* patterning during materials growth. To understand the potential, it is important to study the surface processes resulting from the laser-matter interaction, which have a key influence on the resulting growth mechanisms. In this work, the intensity distribution and the laser-semiconductor interaction resulting from four-beam interference patterns are analysed by numerical simulations. In particular, we derive the time and spatially dependent thermal distribution along with the thermal-induced desorption and surface diffusion. The results provide a crucial understanding of the light-induced thermal profile and show that the surface temperature and the surface adatom kinetics can be controlled by multi-beam pulsed laser interference patterning due to photothermal reactions. The approach has potential as an *in-situ* technique for the fast and precise nanostructuring of semiconductor material surfaces.

1. Introduction

In recent years, various nanopatterning methods have attracted attention in order to fabricate periodic and quasi-periodic nanostructures which exhibit unique optical and electronic properties for potential applications in nanoelectronics, optoelectronics and biomaterials [1-3]. Ordered semiconductor nanostructures especially self-assembled quantum dots (QDs) have emerged as important candidates for novel photonic devices, particularly for the control of single photons for quantum information processing and quantum computing [4,5]. Thus it is highly demanded to fabricate nanostructures with uniformity, ordering and regular positioning. Self-assembly via Stranski-Krastanov growth mode offers a potential way to obtain a large number of nanostructures, but suffers from an inhomogeneous size distribution and a lack of site control [6]. At present, nanopatterning techniques such as electron beam lithography, AFM-based patterning and focused ion beam etching have been applied to pattern semiconductors to enhance the ordering of nanostructures [7-9]. However, many of these techniques suffer from processing contaminants, defects and damage introduced during the nanopatterning processes, as well as having an inherently high equipment cost and a low processing throughput [7]. Therefore, the development of new approaches to pattern the surface of materials at the nanoscale and combining these with the self-assembled growth of nanostructures is of considerable importance.

Laser interference has been demonstrated to be an attractive way for nanopatterning since it is fast, cost-effective and high-efficient. It has the capability to create large-area, defect-free, one-, two- and even three-dimensional ordered nanostructures on a wide variety of materials including semiconductors, metals and polymers [10-12]. Laser interference lithography involving photoresists and etching has been widely employed in the fabrication of semiconductor devices [13-15]. However, the resulting contamination and defects on an atomic scale render the surface non-ideal for subsequent epitaxial growth. For this reason, we have chosen to study the direct (resist-free) patterning of surfaces: a methodology which requires only the application of laser interference to a sample surface in a controlled environment. Such a technique can be compatible with materials reactors (e.g. vacuum chambers) providing the required optical access can be obtained. Whilst the pattern pitch is limited by the wavelength of the light to be in the range 100-200 nm, the non-invasive nature of the technique makes it possible to combine with materials growth and processing equipment in order to modify the materials formation process. The approach has the potential to nucleate a regular array of identical self-assembled structures of sub-10nm dimensions.

Thermodynamic processes resulting from the laser-matter interaction are of crucial importance in understanding the growth mechanisms of nanostructures, since the movements of atoms are the major driving forces of self-assembly process [16-18]. The detailed mechanism of island/dot formation has been the subject of research over the years [19-21]. The laser pulses can interact with the surface through photothermal, mechanical, and photochemical processes leading to surface modifications. Usually the photothermal effect is dominant [22] and in the high energy regime, this results in surface ablation [23]. Single-pulsed and multi-pulsed laser ablation and laser-induced surface damage in semiconductors have been extensively studied [24-26]. However, very few works have studied the lower energy range in which the laser induces a change in surface morphology manifested through a modification of surface adatom kinetics and not through ablation. In this work, we built a model of the surface dynamics of indium during self-assembled InAs/GaAs QDs growth process by *in-situ* four-beam laser interference patterning.

2. *In-Situ* Laser Interference Patterning

In our work, we apply multi-beam laser interference to the direct patterning of semiconductor surfaces within an

MBE growth environment. We aim to make use of the pattern of laser fluence and the resulting surface thermal transients to locally control surface adatom diffusion and desorption processes to nucleate self-assembled nanostructures on a regular pattern. Specifically, we look at the site-controlled growth of InAs/GaAs quantum dots.

To achieve patterning of the growth surface, the thermal timescale must be compatible with the timescales of adatom processes. We have therefore performed time-dependent thermal simulations in this paper and we discuss the results in terms of potential mechanisms for self-assembled nanostructure growth. In this paper, the laser-induced surface thermal gradient and the behaviour of typical surface processes that occur on a GaAs substrate following pulsed laser irradiation using four-beam laser interference (355nm, 7ns pulses, 100mJ pulse energy) are studied by numerical simulations. Our studies start with the calculation of the intensity distribution of four-beam interference which is dependent on the beam parameters. All the work was performed using MATLAB simulations.

3. Theory of Multi-Beam Interference

Multi-beam interference can be considered as a linear superposition of multiple light waves satisfying the wave equation. To simplify the theoretical analysis, the laser beam can be approximated as a uniform plane wave when both the divergence angle and interference area are small. This approximation can be established since we will use a pulsed laser source with a flat-topped beam profile achieved by beam-shaping optics (Spitlight 400, Innolas GmbH).

The total intensity of the interference field of N coherent beams can be written as [27]

$$I = \left|\sum_{i=1}^{n} \vec{E}_i(r)\right|^2 = \left|\sum_{i=1}^{n} A_i \cdot \vec{P}_i \cdot exp\left[i\left(\vec{k}_i \cdot \vec{r}_i - \omega t + \delta_i\right)\right]\right|^2 \quad (1)$$

where A_i is the amplitude, $\vec{P}_i$ is the unit polarization vector, $\vec{k}_i$ is the vector in the propagation direction, $\vec{r}_i$ is the position vector, ω is the frequency and δ_i is the initial phase. In the equation (1), $\vec{P}_i$, $\vec{k}_i$ and $\vec{r}_i$ can be expressed as

$$\vec{P}_i = -(cos\theta_i cos\Psi_i cos\varphi_i - sin\varphi_i sin\Psi_i)\vec{\imath} - (cos\theta_i cos\Psi_i sin\varphi_i + cos\varphi_i sin\Psi_i)\vec{\jmath} - (sin\theta_i cos\Psi_i)\vec{k} \quad (2)$$

$$\vec{k}_i = k(sin\theta_i cos\varphi_i \vec{\imath} + sin\theta_i sin\varphi_i \vec{\jmath} - cos\theta_i \vec{k}) \quad (3)$$

$$\vec{r}_i = x \cdot \vec{\imath} + y \cdot \vec{\jmath} + z \cdot \vec{k} \quad (4)$$

where θ_i represents the angle of incidence, Ψ_i is the polarized angle, φ_i is the azimuth angle, $k = 2\pi/\lambda$ is the wave number and λ is the wavelength of the laser. As for two-beam interference, the pitch P of the interference fringe can be determined by the wavelength of the laser and the incidence angle of beams. It can be calculated by simple geometric considerations.

$$P = \lambda / 2sin\theta \quad (5)$$

By using different wavelengths and/or angles of incidence, the pitch of the pattern can be realized from micro- to nano-metres. Different types of patterns can be yielded by means of selecting different parameters of the beams.

4. Theoretical Analysis and Simulations

4.1. Patterns of Four-beam Laser Interference

In this work, four-beam laser interference using the 2nd harmonic of Nd-YAG at λ=355nm is described. The amplitudes of four beams are assumed to be identical and the initial phases are all zero. When four coherent beams follow a configuration with the same incidence angle of 30° using azimuth angles of 0°, 90°, 180° and 270° and with all the polarized angles at 90° to the plane of incidence, the intensity distribution pattern is shown in Fig. 1(a). Keeping other parameters unchanged, but increasing the incidence angles to 60°, the period of the pattern in Fig. 1(b) decreases to around 200 nm. It is important to point out here that a regular pattern at a pitch of around 200 nm is a challenge for any other lithographic technique since these are subject to drift and proximity effects. Yet for interference lithography this is a relatively simple single-shot exposure process. Fig. 1(c) and (d) illustrate that the polarization state of beams can change the distribution pattern and also affect the contrast of the pattern.

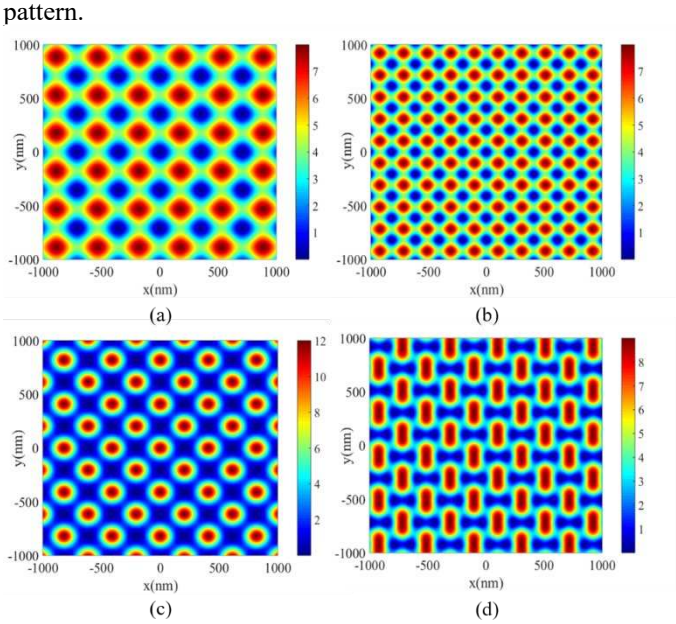

Fig. 1. *The intensity distribution of four-beam interference with* ***(a)*** *identical incidence angles of 30°and polarized angles of 90° (TE mode),* ***(b)*** *identical incidence angles of 60°and TE polarization mode,* ***(c)*** *identical incidence angles of 60°and polarized angles of 0° (TM mode),* ***(d)*** *identical incidence angles of 60° and polarized angles of 90°,0°,90°,0°, respectively (TE-TM mode)*

The simulation results prove that the intensity distribution can be modulated by controlling the incidence angle and the polarization direction. The period of the interference pattern is inversely proportional to the incident angle and the polarization state has a strong influence on the pattern symmetry and contrast. Apart from that, other beam parameters, such as the azimuth angle can also lead to changes of the interference pattern, the relative phase difference results in a shift of the pattern and beam intensity would affect the shape of the patterns [28].

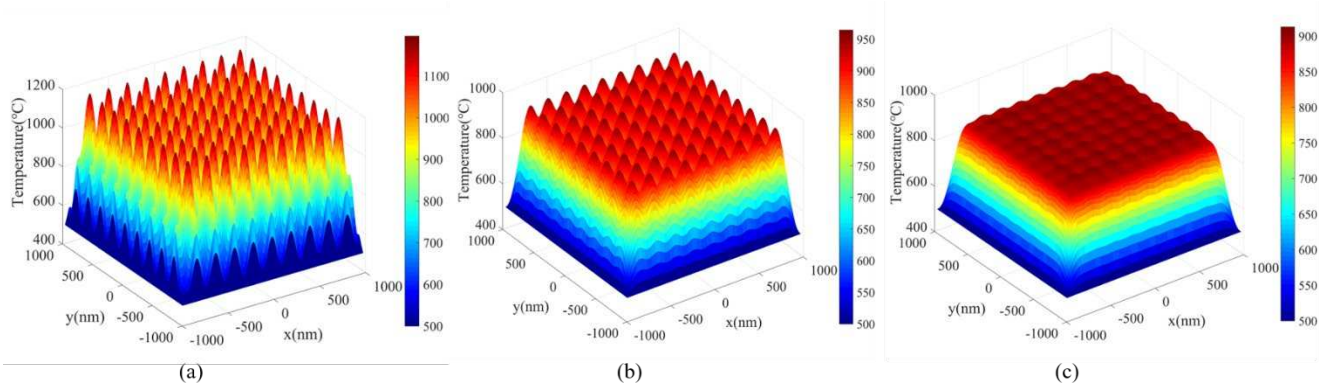

Fig. 2. *Transient temperature distribution of GaAs at different time following pulsed laser irradiation* ***(a)*** *0 ns,* ***(b)*** *50 ns,* ***(c)*** *100 ns*

4.2. Modelling of the Two-dimensional Thermal Transient

The surface irradiated by the laser generates a temperature rise due to the absorption of the laser energy. The thermodynamic properties of laser absorption of the material can be described by the Fourier thermal conduction equation. Irrespective of the phase change and the exact mechanism that affects the absorption, when the material is isotropic and homogeneous, the two-dimensional transient thermal diffusion equation can be expressed as

$$\rho c \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + Q \tag{6}$$

$$Q = (1 - R)\alpha I(x, y, t) \tag{7}$$

where T is the temperature in the substrate at time, ρ is the mass density of GaAs, k is the temperature-dependent thermal conductivity, c is temperature-dependent thermal capacity, Q is the heat source represented here by the laser energy absorbed by the material, R is the surface reflectivity and α is the absorptivity of the laser energy. The spatial intensity distribution $I(x, y, t)$ by four-beam interference of Fig. 1(b) is applied to the thermal calculation.

According to the above calculation model, the transient thermal distribution of a GaAs surface irradiated by a nanosecond laser pulse is solved numerically based on finite-difference method. The parameters used in the calculation are shown in Table 1.

Table 1 Thermo-physical data of GaAs [26] and laser parameters

Parameter (unit)	Value
ρ (g/cm^3)	5.32
c (J/g·K)	$0.307 + 7.25 \times 10^{-5}T$
K (W/cm · K)	$2271/T^{1.463}$
R	0.4
α	0.2
Beam diameter (mm)	6
Laser energy (mJ)	100
Pulse width (ns)	7
Initial temperature T_0(K)	773

As shown in Fig. 2, the four-beam interference exhibits a periodic temperature rise over the surface. The intensity distribution on the surface consequently induces a corresponding spatial distribution of temperature. The temperature of a GaAs surface rises rapidly after pulsed laser irradiation reaching ~1200 °C, but still just below the melting threshold. The highest temperature is sited in the interference maxima. A temperature difference of a few 100 °C exists between the maxima and minima which then slowly equilibrates over a timescale of ~100 ns.

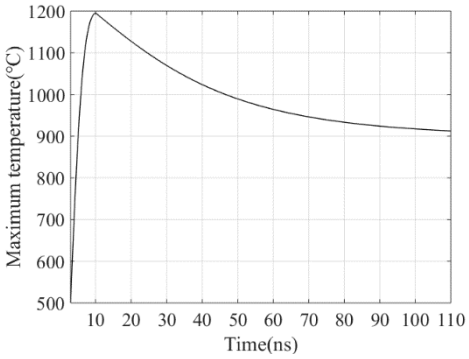

Fig. 3. *Time dependent surface maximum temperature during and after the pulsed laser irradiation.*

Our intention is to use these thermal transients to locally control surface adatom kinetics including both surface diffusion and thermal desorption processes during QD epitaxial growth. To understand these processes, we can start by considering a 1ML thin layer of InAs deposited on the GaAs surface as a precursor for quantum dot nucleation. We may describe this layer as the 2D wetting layer which occurs before the transition to 3D Stranski-Krastanov growth [29]. We assume this initial layer to be a layer of indium atoms absorbed evenly on the GaAs surface, followed by applying pulsed interferometric laser light. We consider at this stage that two processes may occur to the indium atoms; they may desorb from the surface under the influence of the thermal pulse or they may diffuse from regions of high temperature to regions of low temperature.

In terms of desorption, it can be seen from Fig. 4 that the indium desorption rate is proportional to the surface temperature. The indium desorption is a thermally activated process and the desorption rate follows the Arrhenius law can be expressed as [30-32]

$$R = Aexp^{-E_a/kT} \tag{8}$$

where A is the pre-exponential factor, E_a is the activation energy of the indium desorption process, k is Boltzmann's constant, T is the substrate temperature in Kelvin. The values of $A = 10^{13} s^{-1}$ and $E_a = 3.5\ eV$ are used in the calculation [31-33]. Fig. 4 indicates that indium adatoms may desorb from the surface due to the elevated temperature at the interference maxima. But after calculations, in terms of a single laser pulse, indium adatoms do not undergo desorption process within the thermal timescale (~ns) due to the relatively longer lifetime of an adatom being evaporated, while it shows obvious thermal desorption after 0.1 seconds continuous laser irradiation. Therefore, it suggests that single-pulsed laser would not induce significant thermal desorption. Without regard to the desorption, we assume the growth mechanism can be attributed to the diffusion process.

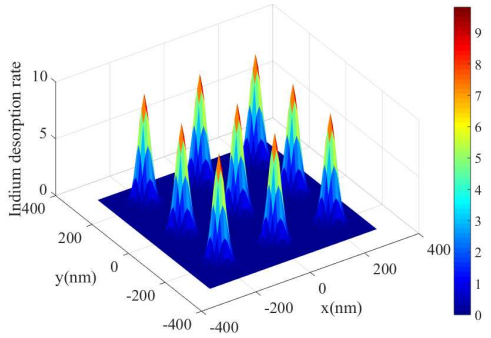

Fig. 4. *The indium desorption rate distribution just after pulsed laser irradiation*

For surface diffusion, we need to consider the flow of indium atoms on the surface, instead of the flow of indium atoms from the surface to the vapour, where the indium atoms are relatively mobile compared with gallium atoms. The diffusion process is a thermally activated random movement of an adsorbate on the surface, in this case indium adatoms jumping thermally from an absorption site to another one [34]. The diffusion equation can be written as

$$D = D_0 exp^{-E_d/kT} \qquad (9)$$

where D_0 is the diffusion coefficient, E_d is the barrier energy of the indium diffusion process, k is Boltzmann's constant, and T is the substrate temperature in Kelvin. The values of $D_0 = 10^{-2} cm^2 s^{-1}$ and $E_d = 0.5\ eV$ are taken from the calculations of Rossini et al and are also consistent with expected ranges for these parameters [34,35]. It is assumed that the initial indium concentration is $2.78 \times 10^{14}/cm^3$ and evenly distributed over the surface.

In our case, the adatoms are assumed to diffuse according to a certain regular trajectory. The simulation results are presented in Fig. 5. As can be seen, the indium surface diffusion performs an inverse relationship with surface temperature i.e. they diffuse from the high-temperature region to the low-temperature region. According to the growth kinetics during MBE growth, clusters or islands would be formed by the aggregation of diffused atoms, promoting the nucleation process [16,18]. Although we have not yet studied the precise nucleation process, the expectation would be that at high concentrations the indium clusters, effectively inducing nucleation at the periodic interference minima and resulting in a periodic array of quantum dots.

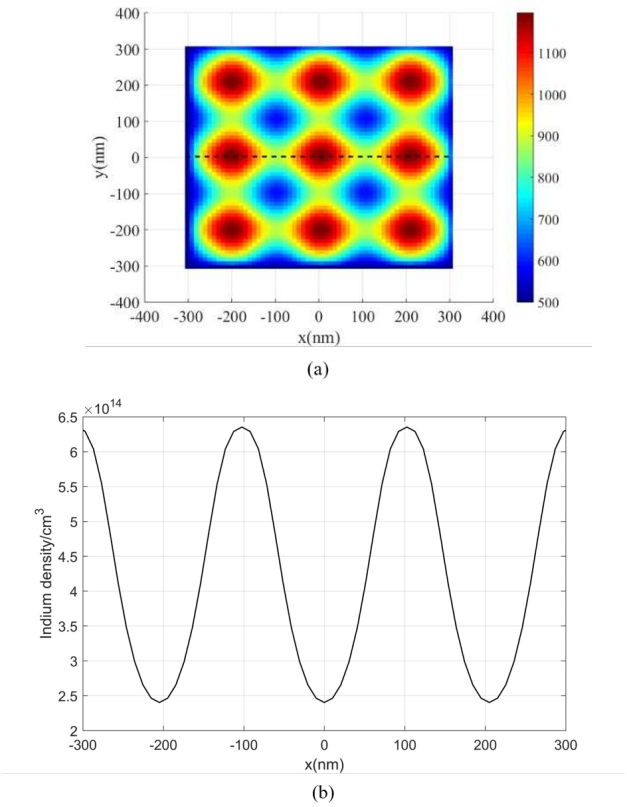

Fig. 5. (a) *Surface temperature distribution after laser pulse,* ***(b)*** *Corresponding calculated indium concentration distribution 100 ns after the pulsed laser irradiation*

5. Conclusion

We have developed a theoretical model that predicts the thermal response of a GaAs wafer after nanosecond pulsed laser irradiation by four-beam laser interference patterning and have simulated the effect on the desorption and diffusion of an indium layer, which is a precursor to InAs quantum dot growth. The intensity distribution of interference can be determined by the parameters of the laser beams, including angle of incidence and the polarization state. The thermal effect of the substrate surface in the presence of desorption and surface diffusion processes is calculated numerically. The temperature increases resulting from the absorption of the incoming pulsed laser. The simulation results show the possibility that the surface thermal effect could induce a tailoring the surface morphology of semiconductor materials by multi-beam interference patterning and suggest a novel and promising technique to create controllable periodic nanostructures during the semiconductor growth process. By considering conditions typical of the MBE growth of InAs quantum dots, we show the possibility that a precise array of such nanostructures could be achieved by nucleation at the interference minima. The results show the potential for *in-situ* multi-beam laser interference as a direct method for the production of arrays of nanostructures without the need for photoresist.

6. Acknowledgments

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7. References

[1] Makeev, M.: 'Self-Organized Quantum Dot Superstructures for Nanoelectronic and Optoelectronic Applications', *Journal of Nanoelectronics and Optoelectronics*, 2006, 1(2), pp. 176-193

[2] Leung, S., Zhang, Q., Xiu, F., et al.: 'Light Management with Nanostructures for Optoelectronic Devices', *The Journal of Physical Chemistry Letters*, 2014, 5(8), pp. 1479-1495

[3] Luo, Q., Hou, C., Bai, Y., et al.: 'Protein Assembly: Versatile Approaches to Construct Highly Ordered Nanostructures', *Chemical Reviews*, 2016, 116(22), pp. 13571-13632

[4] Hirayama, Y., Miranowicz, A., Ota, T., et al.: 'Nanometre-scale nuclear-spin device for quantum information processing', *Journal of Physics: Condensed Matter*, 2006, 18(21), pp. S885-S900

[5] Kloeffel, C. and Loss, D.: 'Prospects for Spin-Based Quantum Computing in Quantum Dots', *Annual Review of Condensed Matter Physics*, 2013, 4(1), pp. 51-81

[6] Kiravittaya, S., Rastelli, A. and Schmidt, O.: 'Advanced quantum dot configurations', *Reports on Progress in Physics*, 2009, 72(4), p. 046502

[7] Vieu, C., Carcenac, F., Pépin, A., et al.: 'Electron beam lithography: resolution limits and applications', *Applied Surface Science*, 2000, 164(1-4), pp. 111-117

[8] Kim, Y., Na, K., Choi, S., et al.: 'Atomic force microscopy-based nano-lithography for nano-patterning: a molecular dynamic study', *Journal of Materials Processing Technology*, 2004, 155-156, pp. 1847-1854

[9] Wang, K., Chelnokov, A., Rowson, S., et al.: 'Focused-ion-beam etching in macroporous silicon to realize three-dimensional photonic crystals', *Journal of Physics D: Applied Physics*, 2000, 33(20), pp. L119-L123

[10] Zhang, J., Venkataramani, S., Xu, H., et al.: 'Combined topographical and chemical micropatterns for templating neuronal networks', *Biomaterials*, 2006, 27(33), pp. 5734-5739

[11] Joannopoulos, J.D., Villeneuve, P.R., and Fan, S.: 'Photonic crystals: putting a new twist on light', *Nature*, 1997, 387(6635), pp. 830-830

[12] Lasagni, A., Bieda, M., Wetzig, A., et al.: 'Direct laser interference systems for the surface functionalization of powertrain components', *Proc. Global Powertrain Congress, 2011,* pp. 167-178

[13] Xuan, M., Dai, L., Jia, H., et al.: 'Fabrication of large-area nano-scale patterned sapphire substrate with laser interference lithography', *Optoelectronics Letters*, 2014, 10(1), pp. 51-54

[14] Domínguez, S., García, O., Ezquer, M., et al.: 'Optimization of 1D photonic crystals to minimize the reflectance of silicon solar cells', *Photonics and Nanostructures - Fundamentals and Applications*, 2012, 10(1), pp. 46-53

[15] Ren, Z., Kan, Q., Ran, G., et al.: 'Hybrid single-mode laser based on graphene Bragg gratings on silicon', *Optics Letters*, 2017, 42(11), p. 2134

[16] Zhang, Z.: 'Atomistic Processes in the Early Stages of Thin-Film Growth', *Science*, 1997, 276(5311), pp. 377-383

[17] Ishii, A., Fujiwara, K. and Aisaka, T.: 'Dynamics of In atom during InAs/GaAs(001) growth process', *Applied Surface Science*, 2003, 216(1-4), pp. 478-482

[18] Ratsch, C. and Venables, J.: 'Nucleation theory and the early stages of thin film growth', *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2003, 21(5), pp. S96-S109

[19] Barabási, A.: 'Thermodynamic and kinetic mechanisms in self-assembled quantum dot formation', *Materials Science and Engineering: B*, 1999, 67(1-2), pp. 23-30

[20] Osipov, A., Kukushkin, S., Schmitt, F. and Hess, P.: 'Kinetic model of coherent island formation in the case of self-limiting growth', *Physical Review B*, 2001, 64(20)

[21] Chiu, C., Huang, Z. and Poh, C.: 'Formation of Nanostructures by the Activated Stranski-Krastanow Transition Method', *Physical Review Letters*, 2004, 93(13)

[22] Sanz, M., Rebollar, E., Ganeev, R., et al.: 'Nanosecond laser-induced periodic surface structures on wide band-gap semiconductors', *Applied Surface Science*, 2013, 278, pp. 325-329

[23] Hendow, S. and Shakir, S.: 'Structuring materials with nanosecond laser pulses', *Optics Express*, 2010, 18(10), p. 10188

[24] Srivastava, P., Pratap Singh, A. and Kapoor, A.: 'Theoretical analysis of pit formation in GaAs surfaces in picosecond and femtosecond laser ablation regimes', *Optics & Laser Technology*, 2006, 38(8), pp. 649-653

[25] Garg, A., Kapoor, A. and Tripathi, K.: 'Laser-induced damage studies in GaAs', *Optics & Laser Technology*, 2003, 35(1), pp. 21-24

[26] Craciun, V. and Craciun, D.: 'Thermal mechanisms in laser ablation of GaAs', *Applied Surface Science*, 1997, 109-110, pp. 312-316

[27] Hariharan, P.: 'Optical interferometry' (Academic Press, New York, 1985, 2nd edn. 2003)

[28] Liu, Q., Duan, X. and Peng, C.: 'Novel optical technologies for nanofabrication' (Springer, New York, 2014)

[29] Wu, J. and Jin, P.: 'Self-assembly of InAs quantum dots on GaAs (001) by molecular beam epitaxy', *Frontiers of Physics*, 2015, 10(1), pp. 7-58

[30] Colayni, G. and Venkat, R.: 'Growth dynamics of InGaAs by MBE: process simulation and theoretical analysis', *Journal of Crystal Growth*, 2000, 211(1-4), pp. 21-26

[31] Heyn, C., Endler, D., Zhang, K., et al.: 'Formation and dissolution of InAs quantum dots on GaAs', *Journal of Crystal Growth*, 2000, 210(4), pp. 421-428

[32] Mozume, T. and Ohbu, I.: 'Desorption of Indium during the Growth of GaAs/InGaAs/GaAs Heterostructures by Molecular Beam Epitaxy', *Japanese Journal of Applied Physics*, 1992, 31 (Part 1, No. 10), pp. 3277-3281

[33] Wang, Z. and Seebauer, E.: 'Estimating pre-exponential factors for desorption from semiconductors: consequences for a priori process modeling', *Applied Surface Science*, 2001, 181(1-2), pp. 111-120

[34] Rosini, M., Righi, M. C., Kratzer, P., et al.: 'Indium surface diffusion on InAs (2× 4) reconstructed wetting layers on GaAs (001)', *Physical Review B*, 2009, 79(7), 075302

[35] Seebauer, E. G. and Allen, C. E: 'Estimating surface diffusion coefficients', *Progress in Surface Science*, 1995, 49(3), pp. 265-330