

Raman spectroscopy investigation on excimer laser annealing and thickness determination of nanoscale amorphous silicon

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2004 Nanotechnology 15 658

(<http://iopscience.iop.org/0957-4484/15/5/043>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 155.69.4.4

This content was downloaded on 11/12/2013 at 04:07

Please note that [terms and conditions apply](#).

Raman spectroscopy investigation on excimer laser annealing and thickness determination of nanoscale amorphous silicon

Y P Zeng¹, Y F Lu², Z X Shen¹, W X Sun¹, T Yu¹, L Liu¹,
J N Zeng³, B J Cho³ and C H Poon³

¹ Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

² Department of Electrical Engineering, University of Nebraska, Lincoln, NE 68588-0511, USA

³ Laser Micro-processing Laboratory, Department of Electrical and Computer Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore

E-mail: ylu2@unl.edu (Y F Lu) and physzx@nus.edu.sg (Z X Shen)

Received 25 September 2003

Published 22 March 2004

Online at stacks.iop.org/Nano/15/658 (DOI: 10.1088/0957-4484/15/5/043)

Abstract

Raman spectroscopy was used to investigate excimer laser annealing and thickness determination of amorphous silicon (a-Si) layers which are less than 20 nm thick. The a-Si layers were produced on silicon (Si) substrates using Si⁺ ion implantation with an energy of 10 keV and a dose of $1 \times 10^{15} \text{ cm}^{-2}$. Excimer laser annealing was applied to re-crystallize the a-Si layers. The dependence of re-crystallization on laser fluence was investigated using Raman spectroscopy. A threshold laser fluence of 0.4 J cm^{-2} was required to re-crystallize the a-Si layers. In Raman spectroscopy, the Raman intensity shows a periodical variation with a period of 90° as a function of the angle between the Si orientation and the laser polarization. Based on this phenomenon, a method to determine nanoscale a-Si film thickness was proposed in two ways. One way was carried out without sample rotation to determine the a-Si thickness provided that the reference c-Si and a-Si/c-Si samples are in the same crystal orientation. The other way was carried out with sample rotation to determine the a-Si thickness without knowing the crystal orientation beforehand.

1. Introduction

With the reduction of circuit geometries in ULSI (ultra-large scale integration), ultra-shallow pn junctions play a key role in the performance of MOSFETs (metal–oxide–semiconductor field effect transistors). Pre-amorphization implantation (PAI) was introduced as a means of minimizing or eliminating the channelling effect in impurity implantation. Ion implantation as a space-conserving method of doping wafers was a useful tool to control the amounts of impurities. However, the high-energy ion beams cause damage to the crystalline surfaces which require post-annealing [1]. Furnace annealing, rapid

thermal annealing and laser annealing techniques have been developed for this purpose [2, 3]. The excimer laser annealing technique has been studied as a promising option [4–6], since the excimer laser has larger beam size and better density homogeneity than other lasers. In addition, the crystallization of a-Si can be carried out with low damage to the substrate, since the light absorption of a-Si is strong in the UV range of the excimer laser wavelengths. Therefore, laser heating is limited to a thin surface layer. As the melting point of a-Si is lower than that of c-Si [7], pn junctions formed by laser annealing would be confined in the a-Si layer. Therefore, a precise, fast and non-destructive way to measure

the thickness of a-Si is needed to determine the junction depth [19].

Raman spectroscopy is a powerful tool to investigate the optical properties of semiconductors [8]. Smith and his co-workers obtained the first Raman spectra of amorphous Si as well as a number of related amorphous semiconductors [9]. Two general and non-trivial physical implications were drawn. One is that the first-order Raman spectrum covers the entire vibrational energy range, whereas for the corresponding crystal state only one zone centre optical phonon is Raman active. The other is that not only does the observed Raman spectrum show the gross features of the entire amorphous vibrational density of states, but the amorphous density of states is very similar to that of the corresponding crystal [10]. It was observed that as the crystalline material becomes amorphous, the Raman scattering cross section changes, resulting in a change in the overall intensity of the corresponding Raman peaks. Samples prepared with different methods show a variability of results [11]. Maley [12] showed experimental data and comparison with theoretical results for polarized and fully polarized components of Raman spectra of variably ordered a-Si films. For heavy doses of order 10^{15} ions cm^{-2} or greater, a continuous amorphous layer is formed on the surface of a target crystal. Nakashima and Hangyo noted that Raman scattering can be widely used to examine damage that accompanies this kind of ion implantation, and can determine the effectiveness of annealing schemes.

Raman spectroscopy has also been widely used as a thickness monitor for many years ago. Dhamelincoart *et al* [13] has shown that it was possible to quantitatively measure sample thickness down to 10 nm based on the signal from a good quality non-resonant Raman spectrum. Raman scattering has also been used as a tool for online monitoring of the molecular beam epitaxial growth of semiconductor based multilayer systems. It shows the possibility of chemical information as well as temperature and layer thickness determination [14]. Combined analysis of Raman peak position and intensity indicates a graphic structure for film thickness of less than 10 nm [15].

In this study, we investigated the re-crystallization of a-Si by excimer laser annealing using Raman spectroscopy. It was found that the c-Si Raman peak intensity increases with laser fluence. The results also showed the sharpening of the Si Raman peak as the a-Si became crystallized. Furthermore, Raman spectra of the Si substrates with and without an a-Si layer were measured using three different excitation light wavelengths. A method to calculate the thickness of the a-Si layer was developed, which gives further information on pn junction depth.

2. Experimental details

(100) n-type c-Si wafers were implanted with Si^+ at a dose of 1×10^{15} cm^{-2} and an energy of 10 keV. Samples with a thin a-Si layer were thus prepared. c-Si wafers without implantation were used as reference samples. The amorphous layers were crystallized using a KrF excimer laser annealing at a wavelength of 248 nm. Laser fluences of 0.2–0.5 J cm^{-2} were used in this study. The pulse width of the laser beam was 23 ns and the repetition frequency was 1 Hz. In the laser annealing,

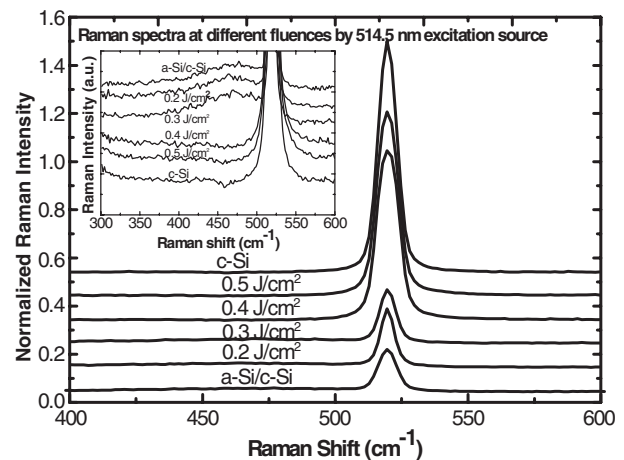


Figure 1. Raman spectra of an as-implanted sample and laser annealed samples in comparison with c-Si by a 514.5 nm excitation light source (the amorphous silicon sample was prepared with a Si^+ dose of 1×10^{15} cm^{-2} at the implantation energy of 10 keV).

a single pulse of the laser beam irradiated each sample surface at room temperature in ambient air. The pre-annealed samples and laser-annealed samples were studied by Raman spectroscopy at room temperature. The Raman experiment was carried out with a spectrometer with a model number of JY T64000. The scattering geometry is backscattering. The integration time was 10 s. Backscattering excited by an argon laser was analysed with an objective lens with a magnification of 50. The excitation laser power is 20 mW for a wavelength of 514.5 nm. Three different wavelengths of excitation light sources (488, 514.5 and 632.8 nm, respectively) were used. In order to determine the thickness of a-Si layers, Raman spectroscopy was carried out on the c-Si and a-Si/c-Si samples in two different ways. One way is to place the samples on the stage without rotation. The other way is to rotate the samples using a rotational stage with a step of 1° to obtain the Raman intensity. Ellipsometry was used to measure the a-Si samples to obtain the extinction coefficient and thus get the absorption coefficient. The transport of ions in matter (TRIM) simulation was performed to estimate the projected range of the 10 keV Si^+ PAI, which confirms our calculated results based on Raman spectroscopy.

3. Results and discussions

3.1. Re-crystallization

Figure 1 shows typical Raman spectra of samples obtained before and after laser annealing under different laser fluences.

First of all, as shown in the insert of figure 1, there is a broad peak belonging to a-Si in the range 480–520 cm^{-1} for the pre-annealed sample and samples annealed at the fluences of 0.2 and 0.3 J cm^{-2} . There is no peak in this range for the samples annealed with higher fluences. The broad peak corresponds to the amorphous-like Si [16, 17]. This means that the fluences of 0.2 and 0.3 J cm^{-2} are not sufficient to re-crystallize the amorphous layer while 0.4 and 0.5 J cm^{-2} are.

The Raman signature of c-Si is mainly composed of a strong narrow peak located at 520 cm^{-1} . Its intensity is

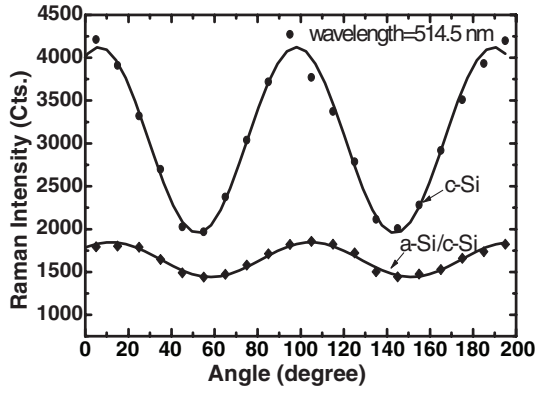


Figure 2. Raman intensity of a-Si/c-Si and c-Si as a function of laser polarization direction (the amorphous silicon sample was prepared with a Si⁺ dose of $1 \times 10^{15} \text{ cm}^{-2}$ at the implantation energy of 10 keV).

stronger for the samples annealed at 0.4 and 0.5 J cm^{-2} , whereas it is much weaker for the samples annealed at 0.2 and 0.3 J cm^{-2} . Although there is an amorphous layer for the samples annealed at low fluences, the a-Si layer is so thin that the laser can pass through the amorphous layer and reach the c-Si substrate that gives rise to the peak at 520 cm^{-1} .

In order to measure the crystal orientation of the laser-annealed samples, x-ray diffraction (XRD) spectroscopy was also performed on these samples. However, no difference was observed among all samples. Only the c-Si peak was observed from all samples. The reason is that the a-Si layer is so thin that the collected x-ray signal is mainly composed of a signal from the c-Si substrates. It shows the advantage of using Raman spectroscopy to characterize the nanoscale a-Si thin films as compared with other methods such as XRD and Rutherford back scattering (RBS).

3.2. Raman intensity

Since the Raman peak at 520 cm^{-1} appears from all the samples (because the amorphous layer is so thin that the laser light could go through only with some attenuation), the intensity can be used to obtain the thickness of a-Si layers. As described above, the Raman spectroscopy was carried out in two ways. The first way is to place the samples directly on the stage if the crystal orientation is known. The other way is to rotate the samples with a rotation stage if the crystal orientation is unknown beforehand or both of these samples have different crystal orientations, because Raman intensity for c-Si is dependent on the angle between the laser polarization and crystal orientation.

Figure 2 shows the Raman intensity as a function of the angle between the laser polarization and the silicon [100] direction from 0° to 180° with the excitation wavelength at 514.5 nm . The intensity of both the a-Si/c-Si and c-Si samples at 520 cm^{-1} showed a variation with a period of 90° . This is due to the factor $\cos 4\theta$ (see below) in the expression of the Raman intensity for the diamond-structured silicon where θ is the angle between x -component of the laser polarization and the silicon [100] direction; see the graph in the appendix (figure 3). The value at 520 cm^{-1} is utilized to determine the thickness of a-Si on the top since a-Si is simply considered as an attenuation layer at this peak.

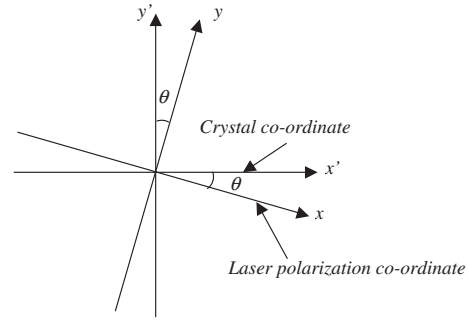


Figure 3. The relationship between the crystal coordinate and the laser polarization coordinate.

For (001) Si, the Raman tensor is $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ [18], assuming that the electrical field of the incident laser signal is $(E_0 \ 0 \ 0)$. Because the light is passing through z direction in the experiment, we only consider the Raman tensor in the x - y plane, and we have $\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} E_0 \\ 0 \end{pmatrix} = \begin{pmatrix} dE_0 \sin 2\theta \\ dE_0 \cos 2\theta \end{pmatrix}$ (θ is as defined above). Matrix $\begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}$ is multiplied for the in-coming laser signal from its original co-ordinate to change into the crystal co-ordinate, then we multiply by $\begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix}$ to let the laser interact with the crystal. After that, we multiply by matrix $\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$ to let the emerging Raman signal from the crystal co-ordinate to change back into the original co-ordinate. The reason why the matrix $\begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}$ has such a form is easy to derive from the graph we drew because $E_{x'} = E_x \cos \theta + E_y \sin \theta$ and $E_{y'} = -E_x \sin \theta + E_y \cos \theta$. Substituting θ with $-\theta$ into the matrix $\begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}$, we can get the matrix $\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$.

Since the spectrometer has different responses in the x and y directions, we set constants k and 1 as the factors of Raman intensity, respectively. (If k equals 1 , then the intensity of the scattered light is not dependent on θ . This is true theoretically, but not true in the experiment because for a spectrometer, responses to the x and y directions are not the same.)

Therefore, we get

$$\begin{aligned} E_x &= kdE_0 \sin 2\theta & E_y &= dE_0 \cos 2\theta \\ I &= E_x^2 + E_y^2 \\ &= k^2 d^2 E_0^2 \sin^2 2\theta + d^2 E_0^2 \cos^2 2\theta \\ &= \frac{d^2 E_0^2}{2} (1 - k^2) \cos 4\theta + \frac{d^2 E_0^2}{2} (1 + k^2). \end{aligned}$$

The solid curves in figure 2 are the results after cosine-function fitting. The experiment results agree well with the fitting results.

3.3. Calculation of a-Si layer thickness

From the discussion described in the previous section, we propose a scheme to calculate the thickness of the a-Si layers.

For a c-Si sample, let I_{R0} be the Raman scattering intensity in the solid angle that would be collected by the spectrometer if a laser light I_0 interacts with the silicon substrate (I_0 is the intensity of the incident laser). The collected Raman signal I_{R0} is proportional to I_0 .

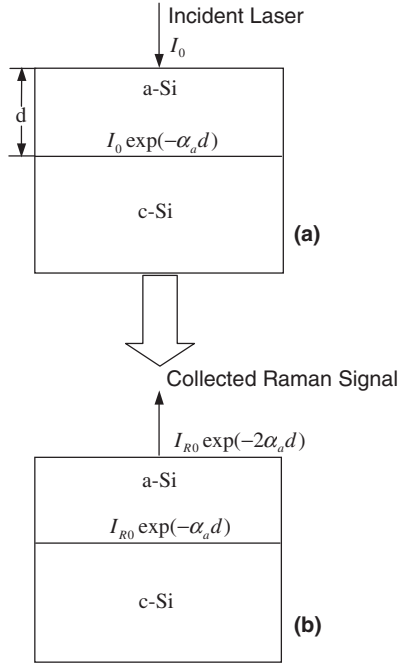


Figure 4. Schematic calculation of the thickness of a-Si/c-Si (a) when the laser is incident (b) when the laser is backscattered.

Figure 4 shows how the incident laser and Raman signal interact with an a-Si layer on a c-Si substrate. α_a and d are the absorption coefficient and thickness of the amorphous layer, respectively. I_1 is the intensity of the laser which passes through the a-Si layer and reaches the a-Si/c-Si interface. We have

$$I_1 = I_0 \exp(-\alpha_a d). \quad (1)$$

Hence, the corresponding Raman signal is proportional to I_1 , which is $I_{R0} \exp(-\alpha_a d)$. When this Raman signal passes through the a-Si layer again, the intensity is reduced for the second time, which is $I_{R0} \exp(-2\alpha_a d)$. (Note that we assume $\alpha_a = \alpha_{\text{Raman}}$, where α_{Raman} denotes the absorption coefficient of the Raman signal by the a-Si, because the wavelength difference is small.)

In order to determine the absorption coefficient of a-Si at different wavelengths, ellipsometry was performed to measure the extinction coefficient. Figure 5 shows the ellipsometry results. The extinction coefficients at 488, 514.5 and 632.8 nm can be obtained. According to $\alpha = \frac{4\pi k}{\lambda}$, the absorption coefficients at different wavelengths could be calculated. The results are shown in table 1.

Therefore, the ratio of collected Raman signal intensity from these two samples is given by

$$\frac{I_a}{I_c} = \exp(-2\alpha_a d) \quad (\text{if experiment is done without rotation}) \quad (2)$$

or

$$\frac{I_{a-\max} - I_{a-\min}}{I_{c-\max} - I_{c-\min}} = \exp(-2\alpha_a d) \quad (\text{if experiment is done with rotation}) \quad (3)$$

where $I_{a-\max}$, $I_{a-\min}$, $I_{c-\max}$, $I_{c-\min}$ are the measured maximum and minimum Raman intensity of a-Si/c-Si and c-Si samples, respectively, which can be taken from figure 2. With

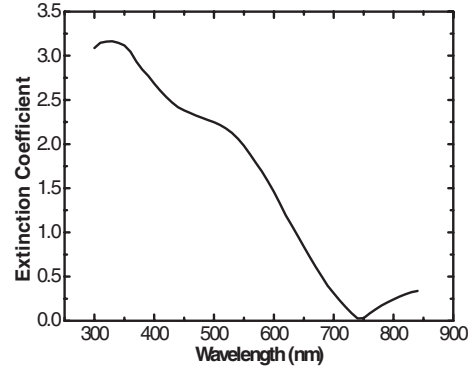


Figure 5. Extinction coefficient as a function of wavelength for a-Si/c-Si by ellipsometry.

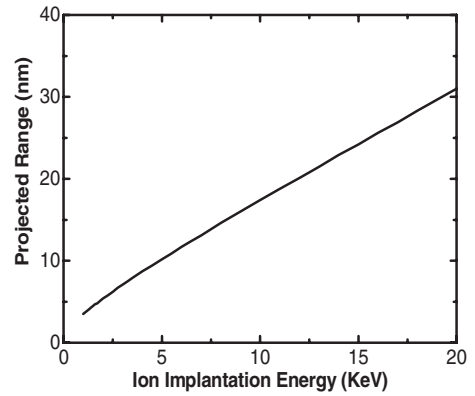


Figure 6. TRIM result of the projected range as a function of ion implantation energy.

Table 1. Thickness determination of amorphous silicon on a silicon substrate.

Parameters used to calculate a-Si thickness			
λ (nm)	488	514.5	632.8
k_a	2.28	2.19	1.077
α_a (nm ⁻¹)	0.0587	0.0534	0.0214
Calculation without rotation with k from ellipsometry result			
$\ln(I_c/I_a)$	2.173	1.876	0.7804
d	18.51	17.56	18.23
Calculation with rotation with k from ellipsometry result			
$\ln\left(\frac{I_{c-\max} - I_{c-\min}}{I_{a-\max} - I_{a-\min}}\right)$	2.023	1.730	0.778
d	17.23	16.20	18.18

equations (2) and (3), the thickness d is obtained, as shown in table 1. The calculated a-Si thickness d without rotation is 18.1 ± 0.36 nm and the result with rotation is 17.20 ± 0.67 nm. It is obvious that both results are consistent with each other.

In order to verify the accuracy in the calculation of a-Si layers, a TRIM simulation was performed to calculate the project range of Si^+ into a silicon substrate. When any ions hit a certain target, they will lose kinetic energy to the collided nuclei and electrons of the material. The extent at which the ions can move will heavily depend on the mass and energy they possess. Figure 6 shows the TRIM simulation results. The project range of 10 keV Si^+ ions in silicon substrates is

about 17.4 nm, which is consistent with the result obtained by other works [19]. The TRIM simulation verifies that our method to calculate the thickness of a-Si layers based on Raman spectroscopy is very precise and feasible. Compared with other methods, such as TEM (transmission electron microscopy) to determine the thickness, Raman spectroscopy has the advantages of being fast and non-destructive.

4. Conclusions

We have used Raman spectroscopy to study the re-crystallization of a-Si by KrF excimer laser annealing. It has been concluded that a laser fluence of 0.4 J cm^{-2} is needed to re-crystallize the amorphous silicon layer. The Raman intensity of the c-Si peak decreases due to attenuation by the amorphous silicon layer. Besides the sharp Raman peak at 520 cm^{-1} due to the c-Si substrate, the samples also show a broad peak of the amorphous phase in the range of $480\text{--}520 \text{ cm}^{-1}$. The intensity of the c-Si Raman peak at 520 cm^{-1} varies with the laser polarization. Based on this phenomenon, a method to calculate the thickness of amorphous silicon was developed. It has been found that the thickness of the a-Si layer of the samples prepared in this study is around 18 nm. Hence, Raman spectroscopy can be used to measure the thickness of a-Si layers on c-Si substrates. This method provides a fast and non-destructive solution to determine the nanoscale thickness of a-Si thin films.

References

- [1] Elliott D J 1995 *Ultraviolet Laser Technology and Applications* (San Diego, CA: Academic) p 209
- [2] Gat A, Gerzberg L, Gibbons J F, Magee T J, Peng J and Hong J D 1978 *Appl. Phys. Lett.* **33** 775
- [3] Serikawa T, Shirai S, Kamaoto A O and Suyama S 1989 *IEEE Trans. Electron Devices* **36** 1929
- [4] Sameshima T, Usui S and Sekiya M 1986 *IEEE Electron Device Lett.* **7** 276
- [5] Sameshima T, Hara M and Usui S 1989 *Japan. J. Appl. Phys.* **28** 1789
- [6] Bachrach R Z, Winer K, Boyce J B, Ready S E, Johanson R I and Anderson G B 1990 *J. Electron. Mater.* **19** 241
- [7] Grigoropoulos C P, Moon S and Lee M 1999 *Appl. Phys. A* **69** S295
- [8] Perkowitz S 1993 *Optical Characterization of Semiconductors: Infrared, Raman and Photoluminescence Spectroscopy* (San Diego, CA: Academic) p 109
- [9] Smith J E Jr, Brodsky M H, Crowder B L, Nathan M I and Princzuk A 1971 *Phys. Rev. Lett.* **26** 642
- [10] Brodsky M H 1983 *Light Scattering in Solids* vol 1, ed M Cardona (Berlin: Springer) pp 210–8
- [11] Brodsky M H 1971 *J. Vac. Sci. Technol.* **8** 125
- [12] Maley N, Beeman D and Lannin J S 1988 *Phys. Rev. B* **38** 10611–22
- [13] Dhmelincourt P, Delhaye M, Tuchet M and Dasilva E 1991 *J. Raman Spectrosc.* **22** 61
- [14] Wagner V, Richter W, Geurts J, Drews D and Zahn D R T 1996 *J. Raman Spectrosc.* **27** 265
- [15] Ohr R and Schug C 2003 *Anal. Bioanal. Chem.* **375** 47
- [16] Watanabe H, Miki H, Sugai S, Kawasaki K and Kioka T 1994 *Japan. J. Appl. Phys.* **1** **33** 4491
- [17] Kim Y H and Hwang C S 2003 *Thin Solid Films* **440** 169
- [18] European Commission, Directorate General, Science, Research and Development 1995 *Catalogue of Optical and Physical Parameters 'Nostradamus' Project*, SMT4-CT95-2024 p 7
- [19] Poona C H, Cho B J, Lu Y F, Zeng J N, Bhat M and See A 2003 Multiple-pulse laser annealing of pre-amorphized silicon for ultra-shallow boron junction formation *J. Vac. Sci. Technol. B* **21** 706