INVESTIGACIÓN Revista Mexicana de Física **57** (2011) 475–480 DICIEMBRE 2011

Refractive index of multiline nanosecond laser-induced periodic surface structures and porous silicon

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Recibido el 21 de junio de 2011; aceptado el 19 de septiembre de 2011

To study the effect of multiline laser processing in the optical response of silicon, a set of p-type single-crystalline silicon wafers with 0.01 to 0.02 Ωm resistivity, 525 μm thickness, and [111] orientation, was irradiated with a multiline Nd:YAG pulsed laser (1064, 532 and 355 nm) applying energies from 310 to 3100 J. A group of those surfaces was produced using argon gas blowing, while other group was manufactured in free atmosphere. Using confocal microscopy, it was observed that the gas-protected samples shown surface periodic structures in the form of ripples with an average pitch of 547 nm. Trough diffuse reflectance tests it was determined that proportionally to the energy supplied in the laser processing, these surfaces reflect between 10% and 30% in the UV region and between 60% and 80% in the IR region. On the other hand, the free atmosphere-made surfaces presented structures and diffraction properties characteristic of porous silicon (PS). The refractive index of the surfaces with periodic structures was calculated based on the diffuse reflectance measures while that of PS surfaces was calculated using the surface voids fraction (pores) determined with the confocal microscope image analysis software.

Keywords: Laser ablation; silicon; periodic structures; porous silicon (PS); refractive index.

Para estudiar el efecto del tratamiento con láser multilínea en la respuesta óptica del silicio, un conjunto de obleas de silicio tipo p monocristalino con resistividad entre 0,01 y 0,02 Ωm, espesor de 525 μm y orientación [111], fue irradiado con un láser Nd: YAG pulsado multilínea (1064, 532 y 355 nm) aplicando energías entre 310 y 3100 J. Un grupo superficies fue producido utilizando soplado con gas argón, mientras que otro grupo fue fabricado en atmósfera libre. Utilizando microscopía confocal, se observó que las muestras protegidas con gas presentaron estructuras de superficie periódicas en forma de ondas con un paso promedio de 547 nm. A través de pruebas de reflectancia difusa, se confirmá que en proporción a la energía suministrada en el tratamiento láser, estas superficies reflejan entre 10% y 30% en la región UV y entre 60% y 80% en la región IR. De otro lado, las superficies tratadas en atmosfera libre presentaron estructuras y propiedades de difracción características del silicio poroso (PS). El índice de refracción de las superficies con estructuras periódicas se calculó con base en las medidas de reflectancia difusa mientras que el de las superficies tipo PS se calculó utilizando la fracción de vacios (poros) en la superficie que a su vez se determinó con el software de análisis de imágenes del microscopio confocal.

Descriptores: Ablación láser; silicio; estructuras periódicas; silicio poroso (PS); índice de refracción.

PACS: 79.20.Eb; 78.20.Ci

1. Introduction

Silicon is an indirect energy gap semiconductor which has been the paradigm of significant advancement in electronics and microelectronics, however the efficiency of the electro-optical response of silicon is low, limiting its use in applications requiring this feature. Some electro-optical responses have been obtained by modifying the silicon surface using different techniques [1-4]. Morphological and structural alterations on the surface of a particular material can also produce changes in its optical, electrical and mechanical properties, which can potentially improve the performance of components made of such material. Through the development of different technologies, there has been success in controlling the morphology and surface structure of materials at different scales. To achieve the required surface modification, the process parameters involved in surface modification must be manipulated, such as the treatment atmosphere, the energy density and the initial surface condition of the material [16-18,20].

For optical components manufacturing, surface texturing processes are widely used in order to obtain diffractive and refractive effects [21-24]. These processes include photolithography, electron beam lithography, grayscale masks, ion beam machining, laser ablation and machining with diamond tools. Common diffractive and refractive optical elements are the diffraction gratings and the zone plates. These elements are used mainly for the separation or combination of electromagnetic beams as required for example in spectroscopic analysis equipment [25-27].

Laser-induced periodic surface structures on metals have been studied in the past using long pulsed lasers. This phenomenon is commonly attributed to the interference between the incident laser light and the excited surface electromagnetic wave [30]. Recently, femtosecond and picosecond lasers have been used to generate periodic surface structures on dielectrics and semiconductors [33].

The silicon material modified with nanoporous holes in its microstructure is known as porous silicon (PS). This kind of silicon has interesting properties such as photoluminescence emission [5-8], high specific surface [9,10] and biocompatibility [9]. Such a material is being used in different applications, including optical waveguides, microcavities, Fabry-Perot type optical devices and gas sensors [9,10,11]. For the above applications and possible new applications, the theoretical explanation for the photonic behavior of PS is currently a topic of great interest and have been proposed several hypotheses, including one that states that this behavior is due to quantum confinement [1-4]. Different processes have been developed for PS manufacturing, among others, cathodic-anodization [1,11], laser-assisted cathodic-anodization [12-14] and laser ablation [15].

To control the laser manufacturing process, there are theoretical models concerning laser-matter interaction to estimate the absorbed energy, the maximum temperature in the absorption region and the material removal rate [16-19]. The power by unit of volume (Q_{abs}) absorbed by a semiconductor irradiated with laser energy can be calculated with Eq. 1 in terms of laser intensity (I), absorption coefficient (A) and depth of the absorbed electric field (l_{abs}). Eq. 2 can be used to determine the maximum temperature (T_m) reached by a laser-irradiated material and whether there is material ablation due to melting. The Eq. 2 terms are: pulse energy (E_{pulse}), radius of beam waist (r_o), specific latent heat of fusion (C) and atomic density (n_a).

$$Q_{\text{abs}} = \frac{2A}{l_{\text{abs}}} I(r, z, t) \tag{1}$$

$$T_m = \frac{2AE_{\text{pulse}}}{Cn_a} \frac{1}{\pi r_o^2 l_{\text{abs}}} = \frac{Q_{\text{abs}}}{Cn_a} \tag{2}$$

In this work were obtained periodic surface structures and PS over p-type silicon surfaces using laser irradiation with a multiline (1064, 532, 355 nm) Nd:YAG pulsed laser. The refractive index (n^{fresnel}) of the laser-induced periodic surface structures was calculated with Eq. 3 [28] using the experimentally measured diffuse reflectance (R_{Si}). For PS surfaces, it was used Eq. 4 [28,29] to calculate the refractive index (n_{PS}) considering the refractive index of single-crystalline silicon (n_{si}) and the fraction of voids (p) present in the treated surface. It should be noted that Eq. 4 is simplified because it does not consider the effect of oxidized silicon.

$$n^{\text{fresnel}} = \frac{\sqrt{R_{Si}} + 1}{\sqrt{R_{Si}} + 1} \tag{3}$$

$$n_{PS} = 0.5\{[2p(1 - n_{Si}^2) - (1 - 2n_{Si}^2)] + [[2p(1 - n_{Si}^2) - (1 - 2n_{Si}^2)]^2 + 8n_{Si}^2]^{0.5}\}^{0.5} \tag{4}$$

Unlike other reported works, the samples were treated with simultaneous radiation of the three laser lines in order to produce combined effects resulting from the differential interaction of each line with the material. Namely line UV (355 nm) is strongly absorbed, the IR line (1064 nm) passes through the silicon without significant attenuation and line VIS (532 nm) has an intermediate behavior [34].

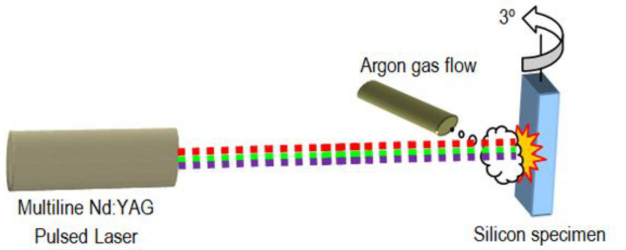

FIGURE 1. Experimental setup.

2. Experimental

2.1. Substrate material and laser irradiation process

To manufacture the surface periodic structures and PS were used polished wafers of p-type silicon (boron doped, single-crystalline, orientation [111]) with 525 μm thickness and 0.01 to 0.02 Ωm resistance. The samples were irradiated by placing them at the beam waist of a Nd:YAG pulsed laser with simultaneous emission on the fundamental (1064 nm) and two harmonic (532 and 355 nm) lines, with pulse energies per line of 900, 450 and 200 mJ, pulse duration per line of 6, 6, and 5 ns, respectively, and repetition rate of 10 Hz. The measured beam diameter at beam waist was 10 mm. Figure 1 is an illustration of the experimental setup.

The irradiation process was carried out with the three lines simultaneous emission and two experimental conditions were used: the first one under free atmosphere and the second one with blowing of argon gas at 275.8 kPa pressure flowing parallel to the irradiated surface. The total energy applied to each surface was adjusted from 310 J to 3100 J with increments of 155 J by controlling the number of laser pulses. To prevent reflection of radiation that could damage the laser cavity as well as to facilitate the expulsion of ablated materials, the samples were tilted so that laser beam impacted at 3° inclination with respect to the surface normal.

2.2. Surfaces characterization

The manufactured surfaces were characterized using a ZEISS M700 confocal microscope and a Cary 5000 UV-VIS-NIR spectrophotometer. The microscope has analytical software to determine the 3D areal surface texture. The parameters measured were the root mean square height of the surface (S_q), and in the case of PS the fraction of voids (p) that appeared in the irradiated surfaces. Using the p values and Eq. 4 it was calculated the refractive index n_{PS} of each PS sample and with the spectrophotometer facilities it was determined the diffuse reflectance (R_{Si}) of the silicon surfaces with laser generated periodic structures in order to calculate its n^{fresnel} refractive index with Eq. 3.

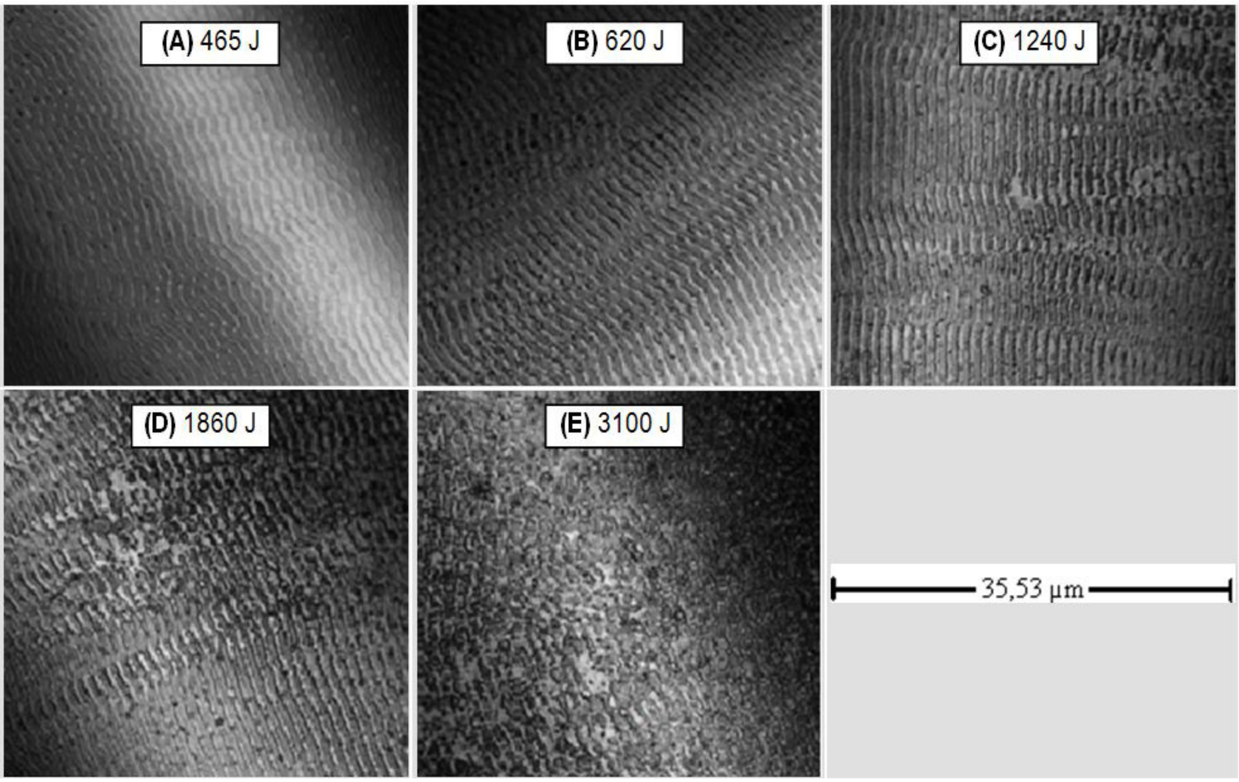

FIGURE 2. Confocal microscope images of samples irradiated with different amounts of energy and argon gas blowing.

3. Results and discussion

3.1. Thermal calculations

For each laser line, the absorption coefficient (A) was estimated from reflectance tests while the depth of the absorbed electric field (l_{abs}) was calculated with Eq. 5 in terms of light speed (c), laser frequency (ω) and the extinction coefficient (k) that was extracted from [34]. Using Eq. 1, it was determined that the specific power absorbed by the silicon material under a single pulse of the used laser is 3×10^{19} W/cm^3. Through Eq. 2, it was calculated a maximum temperature of about 1925 K per laser pulse. This temperature is higher than the fusion point of crystalline Si (1414 K), *i.e.*, the energy supplied in all of the experiments can produce material ablation and thermal changes on the silicon wafers.

$$l_{abs} = \frac{c}{\omega k} \tag{5}$$

3.2. Laser process with gas assistance: periodic structures

Ripples or laser-induced-periodic-surface-structures formation have been reported on various materials. In many cases after irradiation at normal incidence, the period of the observed structure is close to the wavelength of the incident radiation with ripples oriented on same direction of the laser polarization [32]. Figure 2 shows representative results of silicon wafers treated with different amounts of energy from 465 to 3100 J with blowing of 275.8 kPa argon gas flowing parallel to the surface. In these images are observed ripples with 547 $\pm$ 13 nm pitch (near to 532 nm VIS line), it is possible that the UV line was absorbed causing substantial warming while the IR line may have passed through the silicon without significant attenuation. The pitch of the formed structures could be explained by the interaction of VIS line with the solidifying material after it was melted by the UV line.

The surfaces A and B in Fig. 2, where produced in the range of threshold energy for periodic structures formation and presented a clean appearance. Surfaces C and D in the same figure showed well-defined structures but with areas where the material was not completely removed. Possibly, the presence of re-deposited material in these surfaces is due to the fact that gas blowing did not remove efficiently the material ablated during laser irradiation. Figure 2-E shows a sample treated with 3100 J that hardly present the periodic structures observed on the surfaces treated with lower energy levels. These results suggest that there are optimal energy levels (*i.e.* 620 J) in order to generate clean periodic structures. Vorobyev *et al.*, [30] obtained similar structures on metal substrates by scanning them with a femtosecond laser. In this work we have used static irradiation (without scanning) with a multiline nanosecond laser. The effect of surface periodic structures on optical properties of silicon can be clearly seen even with the naked eye as shown in Fig. 3 where the sample irradiated with 620 J total energy exhibit different colors at different viewing angles.

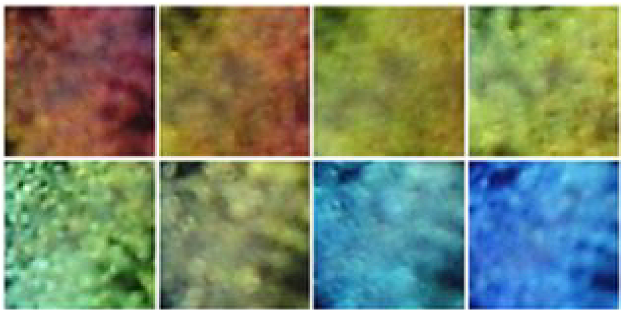

FIGURE 3. Color photographs (3 × 3 mm) at different viewing angles of the sample irradiated with 620 J total energy.

TABLE I. Pitch of the formed periodic structures

Applied energy [J]	Pitch Λ [nm]
620	571
930	547
1240	537
1860	538
2480	533
2790	555
3100	No structures formed

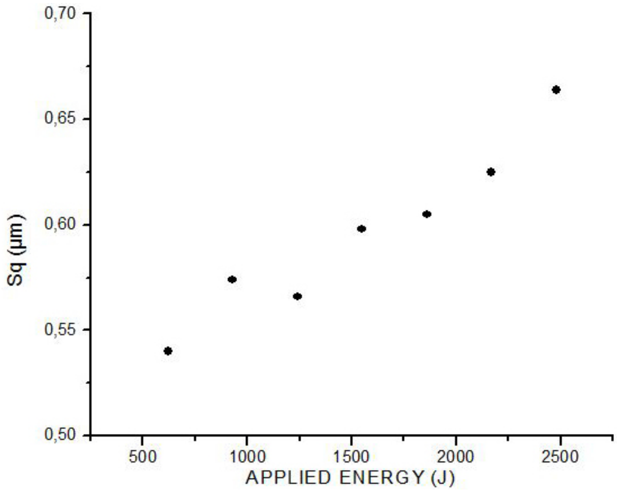

FIGURE 4. Root mean square height (S_q) of the periodic structures as a function of the applied energy.

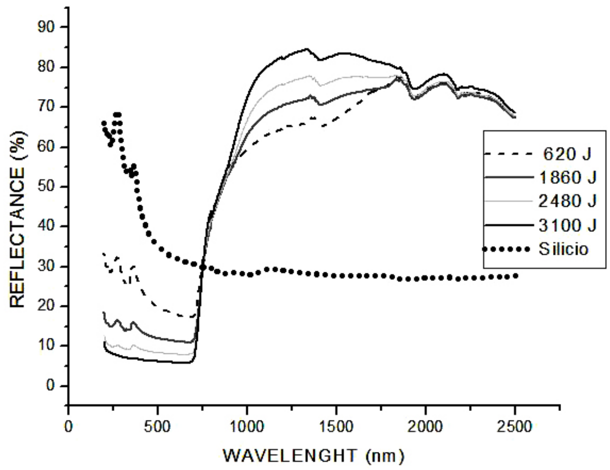

FIGURE 5. Results of diffuse reflectance tests on laser irradiated and on untreated silicon samples.

Using the image analysis software of the confocal microscope, it was measured the pitch (Λ) of the ripples formed for each energy level applied to the samples and the respective results are shown in Table I. The average distance between peaks was 547 $\pm$ 13 nm so clearly the 532 nm line determined the period of the formed structures. This is in agreement with Eq. 6 [32], where Λ represents the pitch of formed structures as function of laser wavelength λ and beam's angle of incidence θ.

$$\Lambda_{\pm} = \frac{\lambda}{1 \pm \sin(\theta)} \tag{6}$$

Figure 4 shows the root mean square height (S_q) values of the fabricated surfaces as a function of the energy supplied to each surface. It can be seen that the depth of the grooves of the structures increases with the amount of energy applied; hence higher energy produces more material removal.

Figure 5 compares the results of reflectance measurements on silicon wafers untreated and treated with different amounts of laser radiation. It can be seen that in the UV region the reflectance of treated surfaces is very low (between 10% and 30%) compared to untreated silicon, while in the wavelength range from 700 to 2500 nm there is a noticeable reflectance increment between 40% and 80%, much higher than that of untreated silicon. For wavelength greater than 1830 nm, it can be seen on the treated surfaces an interfering response (reflectance varies between 68% and 78%). These

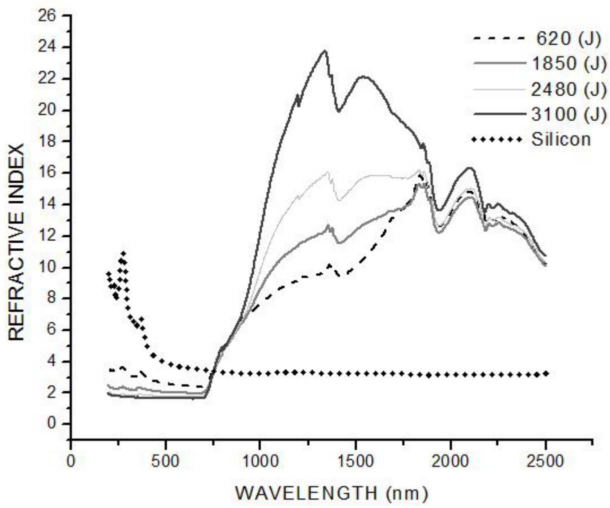

FIGURE 6. Calculated refractive index of untreated silicon and of silicon irradiated with gas assistance.

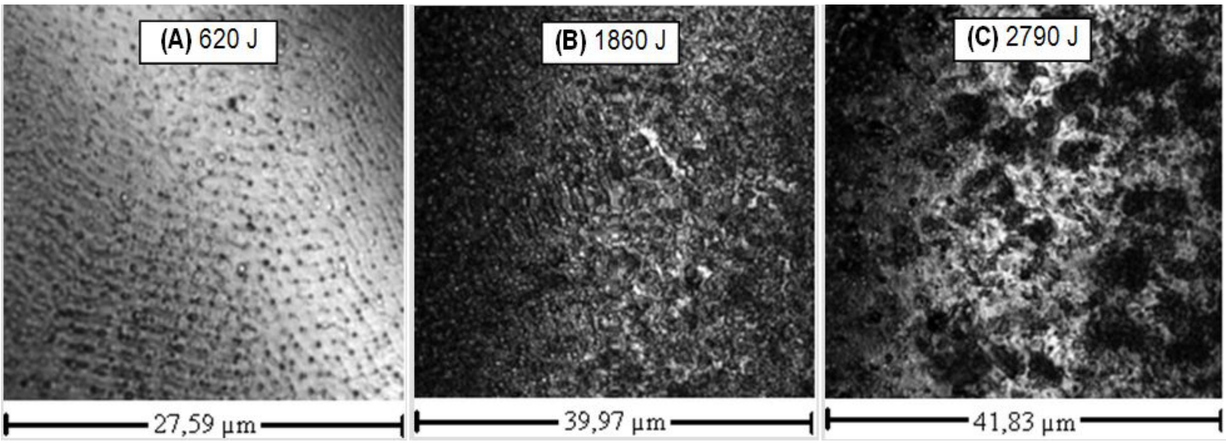

FIGURE 7. Confocal microscope images of samples irradiated without argon gas blowing. Each image is labeled with the energy applied.

TABLE II. Calculated refractive index n_{PS} (at $\lambda = 1200$ nm) of the fabricated PS samples.

Applied energy [J]	n_{PS}
310	2.83
620	3.03
930	1.99
1860	1.74
2790	1.43

These results can be explained by effect of the periodic structures generated on the irradiated surfaces.

Using Eq. 3 with the results of diffuse reflectance tests (Fig. 5), it was calculated the refractive index of each sample. The respective results are shown in Fig. 6, where it can be seen that the refractive index of the treated surfaces varies between 2.2 and 3.5 in the UV and visible bands, and from 2.2 to 23.0 in the IR band. These refraction values are characteristic of metallic materials.

Most of the reports about laser manufacturing of submicron surface periodic structures on silicon are based on ultrafast ps or fs lasers. This work allowed demonstrating the possibility to generate such structures using irradiation process with a multiline ns laser using inert gas assistance.

3.3. Laser process without gas assistance: porous silicon (PS)

Figure 7 shows confocal microscope images of some silicon surfaces that were fabricated using laser irradiation but without inert gas blowing. It can be seen that in (A) there are rough periodic structures while the appearance of the surfaces (B) and (C) is that of PS.

Table II shows the refractive index calculated for the surfaces manufactured without argon gas blowing. To perform the calculation it was used Eq. 4 with the porosity (p) data provided by the image analysis software of the confocal microscope and $n_{Si} = 3.45$ for the real part of the refractive index of monocrystalline silicon at 1200 nm wavelength irradiation [31]. The calculated values are comparable to those reported by Pap *et al.*, [28] who obtained PS by cathodic-anodization process. For porous silicon manufacturing, laser irradiation process has the advantage of producing no waste of chemicals compared to the methods by cathodic-anodization or electrochemical attack.

4. Conclusions

Based on the results obtained in this work, it can be conclude that:

- With nanosecond multiline Nd:YAG laser processing it is possible to produce periodic structures on single-crystalline silicon. To obtain the periodic structures is necessary the assistance of inert gas in order to remove dynamically the ablated material.

- To produce the periodic structures, there is a laser energy threshold. With density energy below threshold, no structure is formed and above threshold there are deposits of re-solidified materials.

- The reflectance of periodic structures obtained on this work differs substantially from the reflectance of crystalline silicon. In the range UV-VIS the reflection decreases when the applied laser energy increases.

- The refractive index calculated in IR range for silicon wafers with periodic structures shows a behavior closer to a metallic material than to a semiconductor material.

- Without inert gas blowing, it is possible to obtain surface structures type porous silicon (PS) by processing the silicon substrates with nanosecond multiline laser. The refractive index of these surfaces is similar to that reported for porous silicon produced by the cathodic-anodization process.

Acknowledgments

The authors gratefully acknowledge the support of the Bogotá Research Division of National University of Colombia under the grants DIB-7178 and DIB-2010100-0001.

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