



ILL record updated to IN PROCESS
Record 94 of 118

ILL pe (N)TK 1871.15.F5 T44
CAN YOU SUPPLY ? YES NO COND FUTUREDATE

Record 88 of 118

:ILL: 4481748 :Borrower: UBY :ReqDate: 20040323 :NeedBefore: 20040422
:Status: IN PROCESS 20040323 :RecDate: :RenewalReq:
:OCLC: 1605925 :Source: OCLCILL :DueDate: :NewDueDate:
:Lender: *UUS,UUM,AZS,AZU,IXA
:CALLNO: *Lender's OCLC LDR: v.123-v.381 1985-2001
:TITLE: Thin solid films.
:IMPRINT: [Lausanne, Switzerland, etc.] Elsevier Sequoia.
:ARTICLE: Osorio-Saucedo, R., Vazquez-Lopez, C., Calleja, W., Allred, D. D.,
Falcony: A rotating electrochemical cell to prepare porous silicon with
different surface structures
:VOL: 338 :NO: 1 :DATE: 1999 :PAGES: 100 - 104
:VERIFIED: <TN:510749><ODYSSEY:128.187.233.109/ILL>OCLC ISSN: 0040-6090
[Format: Serial]
:PATRON: Allred, David D.

:SHIP TO: Brigham Young University ILL
3421 Lee Library
One Lee Lane
Provo, Ut 84602

:BILL TO: same
:SHIP VIA: Ariel :MAXCOST: 20ifm :COPYRT COMPLIANCE: CCL
:FAX: (801) 422-0471, Phone 801-422-3624
:BILLING NOTES: UMI Account Number #D9522701. ISI ACCT: File #0016890 (**ISI SHIP
VIA FEDERAL EXPRESS**)
:BORROWING NOTES: 51-0724 BCR/AMIGOS Code Signer. ARIEL Address:
128.187.229.251 CLient Code ACF17E Please conditional negative replies.
:LENDING CHARGES: :SHIPPED: :SHIP INSURANCE:
:LENDING RESTRICTIONS:
:LENDING NOTES:

**THIS ARIEL IS FOR SENDING ONLY.
IF YOU NEED A RESEND PLEASE
SEND A FAX TO (435) 797-7475.**

THANK YOU.

A rotating electrochemical cell to prepare porous silicon with different surface structures

R. Osorio-Saucedo^a, C. Vázquez-López^{b,c,*}, W. Calleja^d, D.D. Allred^e, C. Falcony^{b,c,f}

^aDepto de Ingeniería Eléctrica del Centro de Investigación y de Estudios Avanzados del I.P.N., Apartado Postal 14-740, Mexico 07300, D.F. Mexico

^bDepto de Física del Centro de Investigación y de Estudios Avanzados del I.P.N., Apartado Postal 14-740, Mexico 07300, D.F. Mexico

^cAlso at Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del I.P.N., Calzada Legaria Num. 694, Col. Irrigación, México 11500, D.F. Mexico

^dInstituto Nacional de Astrofísica, Óptica y Electrónica, Tonantzintla, Pue, Mexico

^ePhysics and Astronomy Department, Brigham Young University, 276 FB, Provo, UT 84602-4636, USA

^fPrograma Multidisciplinario de Ciencias Aplicadas y Tecnología Avanzada del CINVESTAV del I.P.N., Mexico, Mexico

Received 12 February 1998; accepted 19 June 1998

Abstract

The design and performance of an electrochemical apparatus and the process for the preparation of porous silicon with different controlled surface structures is described. The apparatus includes controlled rotation of the electrolyte vessel, which is in contact with a thermal bath. This permits the etching electrolyte to react with the silicon substrate at different temperatures and at different rates of renewal of the solution. Atomic force microscopy images show at least three different classes of samples according to the topographical features: samples with surface hillocks, samples with surface holes, and samples with a mixture of holes and hillocks. The different morphologies are important for various applications. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Atomic force microscopy (AFM); Porous silicon; Nanostructures; Surface morphology

1. Introduction

Porous silicon (PS) is a nanostructured material prepared by various chemical and electrochemical etching processes. Its potential applications in optoelectronics, flat panel displays technology, and as a chemical sensor has generated remarkable interest since the discovery of its light emission properties in 1990 [1].

Depending on the characteristic dimensions of the surface features, PS can be employed as a quantum confinement enhancer, as an antireflecting coating on silicon solar cells [2,3] or it can also be used for chemical sensor applications, in which the effective surface area should be as large as possible [3]. Thus, it is important to control the surface roughness.

The electrochemical cell has been designed and made in various ways in the past. Since the traditional design [4,5], a few improvements have been made only in the sample holding. The control of the process during the etching has not changed. In Table 1 a relation of the six most representative types of electrochemical cells is presented [4–9]. The cell

designed in this work is also included for comparison. Among these designs, the method of wet sample by surface tension of the electrolyte [8] is, maybe, the most interesting, due to the facility of changing samples. Nevertheless, it has the drawback of limiting the renewal of the electrolyte near the surface sample. As for the cells in which the sample is part of the electrolyte container [4–6], the mounting and unmounting procedure is a drawback, because it is time consuming and delicate. In the double wall cell method [7], the sample is fixed to a detachable holder with a window that could obstruct the electrolyte renewal.

In addition to the different designs of electrolytic cells, many methods of PS preparation have been reported, including anodization etching [1], photoinduced etching, stain etching [10], oxidation-etching cycles or simultaneous oxidation-etching process [11], and hydrothermal etching [12]. Sometimes, in these processes, agitation of the solution is used, for example, by magnetic stirring or ultrasonic vibration. In the case of n-type samples, illumination is necessary. Sometimes these methods are combined with post annealing and/or surface modification by reactive ambient processes [11] or relaxing surface stress by freezing techniques [13]. These methods produce high quality

* Corresponding author; e-mail: cvazquez@fis.cinvestav.mx.

Table 1
Different electrolytic cells for preparing porous silicon

Electrolytic cell	Sample holder	Temperature control	Electrolytic renewal near the sample	Main drawback
Traditional I [4]	Sample covers a window of the electrolyte container	Not mentioned	No	Sample is part of the electrolytic cell
Traditional II [5]	Sample covers a circular window of the vessel with an O-ring	Not mentioned	No	Sample is part of the electrolytic cell
Sample between two electrolytic containers [6]	Each sample surface is framed with an O-ring	Not mentioned	No	Sample is part of the electrolytic container
Double wall cell [7]	Detachable from the electrolytic cell	Yes, water circulating between walls	Limited	Electrolyte confinement adjacent to the sample
Wet sample by surface tension of the electrolyte [8]	Vacuum chuck	Not mentioned	Limited	Ohmic contact could be wet by the movement of the electrolyte
Rubber frame [9]	Vacuum chuck	Not mentioned	Not mentioned	Only for large samples, no electrolytic renewal
Present work	Integral arrangement detachable from the vessel	Yes	Yes	See text.

samples for light emission. Few explicitly address how morphology can be controlled. It is generally agreed upon that the kind of porous layer that can be expected depends on current density and doping density of the bulk silicon [14]. The purpose of this paper is to describe the construction and use of a convenient apparatus which includes an efficient control of the electrolyte temperature and of the continuous renewal of the electrolyte near the sample, for the purpose of controlling the surface topographical features of PS. For that purpose, the electrochemical vessel is

immersed in a thermal bath and is designed to rotate at a controlled speed. Afterwards, the etching electrolyte acquires turbulent movement by keeping the substrate, the counter electrode and a pallet attached to the sample holder immobile. The purpose of this electrolyte turbulence is: (1) to control and homogenize the temperature of the electrolyte, (2) to renew the electrolyte adjacent to the sample, (3) to avoid the insulating effect of hydrogen bubbles, and (4) to study the influence on the roughness of the electrolyte momentum.

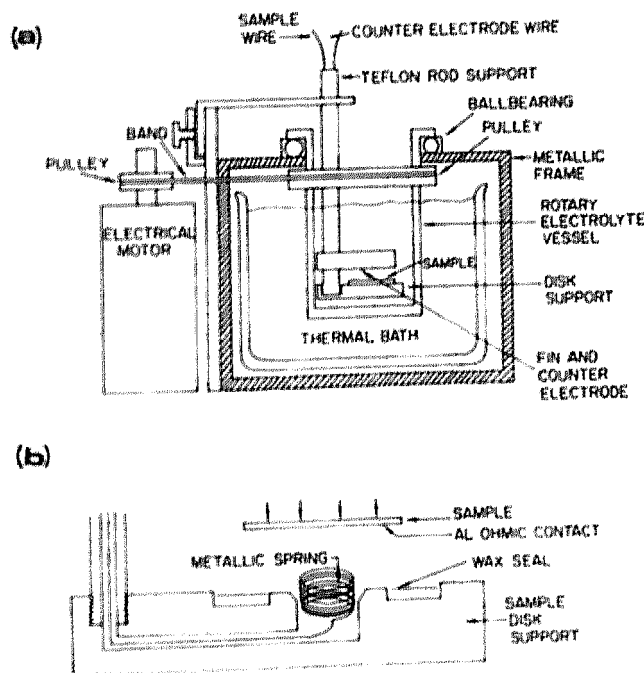


Fig. 1. Experimental set-up for the porous silicon preparation. The vessel diameter is 6 cm

2. Experimental

2.1. The electrochemical cell

The substrates were p-type silicon wafers, with a resistivity of 14–20 ohm cm. To assure an ohmic contact, boron was thermally diffused on the rough surface, and then an aluminium thin film was evaporated on it. Finally, the sample was annealed. The experimental set-up for the PS preparation is shown in Fig. 1. The substrate was glued to a Teflon disk holder with a mixture of high fusion temperature tree wax and an adhesive gum, as shown in Fig. 1b, such that a metallic spring is in electrical contact with the sample ohmic contact (see Fig. 1). The sample holder is attached to a Teflon rod provided with two conductor wires: one for electrical access to the sample and the other for the counter electrode. The necessary heat to fuse the wax mixture was provided by a 300 W tungsten lamp, and was done in such a way that the electrical connection to the sample, the aluminium ohmic contact and the edges were hermetically sealed from the electrolyte. The electrolyte was 49% concentrated HF solution. The counter electrode was a gold-plated grid. The vessel was made of Teflon and during the etching

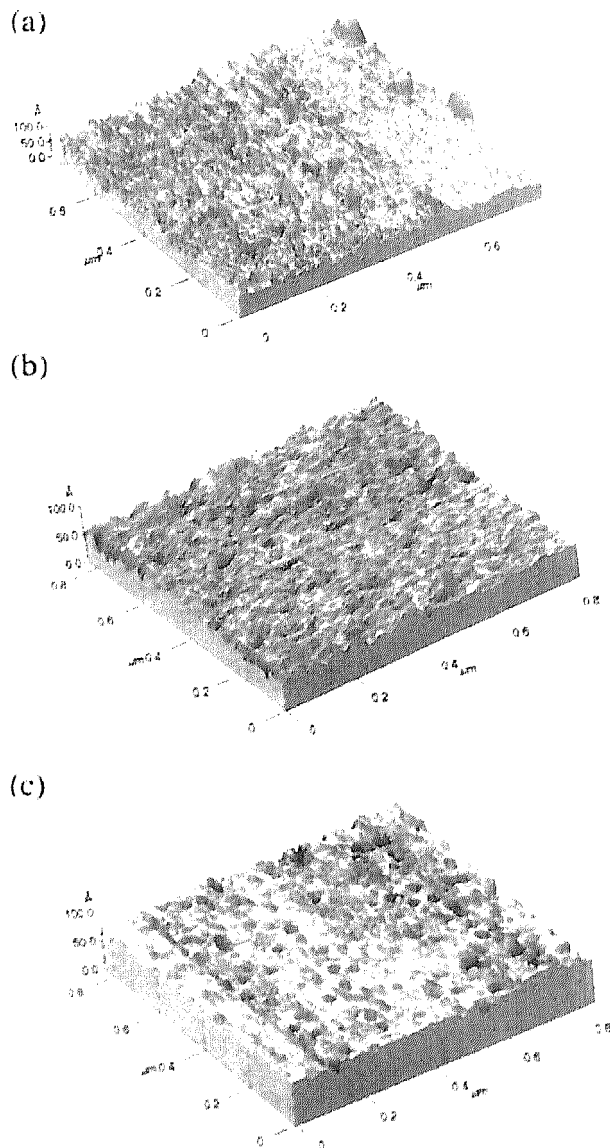


Fig. 2. AFM micrographs of the three different types of morphological features obtained with the apparatus described in Fig. 1 at 10°C. (a) Hillock morphology, rotation rate 10 rev./min; (b) hillocks and holes, rotation rate 40 rev./min; (c) holes obtained at a rotation rate of 80 rev./min.

process was rotated by means of a mechanism made of a ballbearing attached to the upper part of the Teflon vessel and a pulley connected to an electrical motor, as shown schematically in Fig. 1a. A V-shaped Teflon pallet held the counter electrode, and was attached to the same immobile Teflon rod support, as shown in Fig. 1a.

In this report the samples were prepared using a current density of 50 mA/cm² during 10 min. Twenty-four types of samples were prepared at different temperatures and vessel rotation speeds. Temperatures of 2, 10, 20, and 40°C were used for the immersion of the Teflon vessel in the thermal bath. For each temperature value, rotation speeds of 10, 20, 40, 80, 120, and 160 rev./min were applied to the vessel.

2.2. PS Microstructure Study

In Fig. 2 three representative atomic force microscopy (AFM) images are shown corresponding to samples prepared at rotating speeds of 10, 40, and 80 rev./min at 10°C. In Fig. 2a the etching process produces surface hillocks, possibly generated from the surface relief of nanostructured Si columns [15]. In Fig. 2b the surface topography shows a mixed surface with less asperities and the appearance of an incipient porous layer. This corresponds to a smoother surface. Fig. 2c shows the formation of a series of mesopores [14], possibly associated with the removal of some hillocks, as will be discussed later. These effects are described by the analysis of the topographical features of the 24 samples. In Fig. 3 the superficial density of hillocks as a function of temperature for various rev./min is plotted. The trend is clear: The number of hillocks increases to a maximum, and then decreases. This decrease could be explained in terms of the removal of hillocks associated with the rotation of the electrolyte vessel and temperature. The surface RMS roughness defined by

$$\sigma = \frac{\sqrt{\sum_{i=1}^N (z_i - \langle z \rangle)^2}}{N} \quad (1)$$

where N is the number of pixels in the image, z_i is the relative height of pixel i , and $\langle z \rangle$ is the average of pixel heights, is a very sensitive parameter correlated with the temperature and rotation speed, as shown in Fig. 4. As turbulence is increased, an initial decrease of roughness is followed by an increase of roughness. The same behavior occurs for the relative change in effective surface area defined by

$$\Delta S = (SA/PA - 1) \quad (2)$$

where SA is the effective surface area and PA is the projected area. This parameter is plotted in Fig. 5. Then the change of only one sample preparation parameter generates different morphological features, including qualitatively different surfaces. At vessel rotation speeds smaller than 40 rev./min a predomination of hillocks occurs. At rotation velocities larger than 40 rev./min a structure of porous material with diameters of 25 nm, approximately, clearly appears.

Among the potential applications of these morphologies it is worth mentioning: (a) the use of hillock-like structures as antireflecting coatings on silicon solar cells [2,3], or as a medium to produce nanometer scale structures [16]; (b) the use of nanoporous silicon for deep impurity diffusion at low temperature [17], or as a sacrificial material [18] in the preparation of deep cavities useful in sensor devices [19].

Other kinds of morphologies, for example spongy, columnar, or globular, can also be obtained by changing the principal preparation parameters. Such parameters include current density, substrate doping [14], anodized

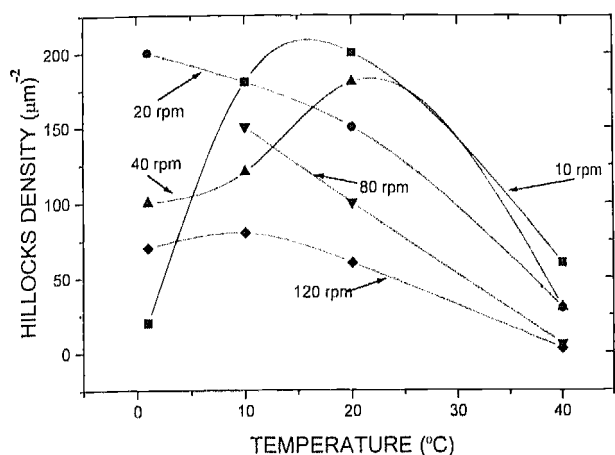


Fig. 3. Surface density of hillocks as a function of temperature for the 24 kinds of samples obtained. The continuous lines serve as guides to the eyes only.

time, light illuminating level, and the electrolyte composition [20]. Thus, a great variety of morphological structures can be prepared by combining the cell proposed in this work with the variation of some of the other sample preparation parameters.

3. Summary and conclusion

In this work a new apparatus of PS preparation has been constructed. This apparatus allows the control of temperature of the etching electrolyte in the range 2–40 $^{\circ}\text{C}$, with an uncertainty of $\pm 1^{\circ}\text{C}$. The rate of the solution renewal at the surface sample is also controlled. Three types of PS surface structures were obtained by varying the vessel rotation speed containing the etching electrolyte: samples with a hillocks like aspect, samples with a mixing of lower hillocks and holes, and samples with a high porosity surface. The hillock density, the roughness, and the relative change of effective area surface were the topographical parameters

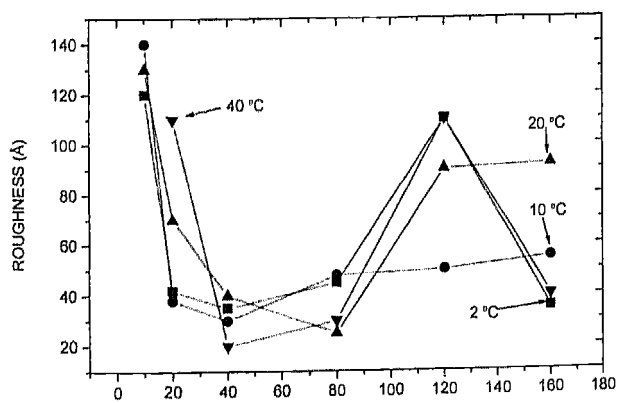


Fig. 4. Surface RMS roughness as a function of vessel rotation speed for different temperatures. The continuous lines serve as guides to the eyes only.

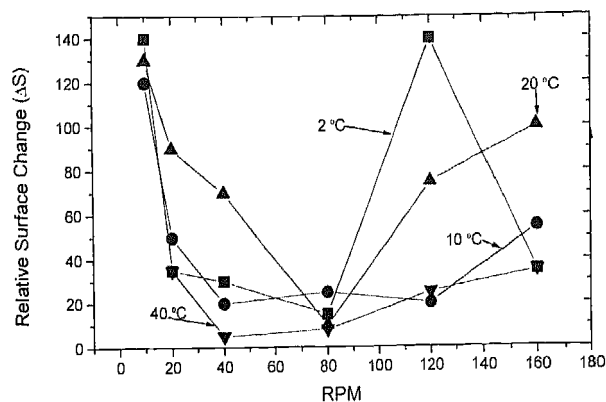


Fig. 5. Relative change of the effective area as a function of the vessel rotation speed. The continuous lines serve as guides to the eyes only.

studied in relation of the samples surface aspect. A general trend of the sample features as the rotation speed is increased consists of an initial decrease of the roughness and the effective surface area, and then, when the vessel speed rotation exceeds 40 rev./min, the roughness and the surface area increase, indicating a different process, which corresponds to a decrease of the density of surface hillocks. Eventually, when the rev./min is large enough to remove hillocks, a hole is left behind. This could explain the porous aspect of the samples.

Acknowledgements

This work was partially supported by Consejo Nacional de Ciencia y Tecnologia (CONACyT, Mexico). The technical assistance of Blanca Zendejas, Rogelio Frago, Angel Castillo, and Marcela Guerrero is also acknowledged.

References

- [1] L.T. Canham, *Appl. Phys. Lett.* 57 (1990) 1046.
- [2] A. Krotkus, K. Grigoros, V. Pacebutas, I. Barsony, E. Vazsonyi, M. Fried, J. Szlufcik, J. Nijs, C. Levy-Clement, *Sol. Ener. Mater. Sol. Cells* 45 (1997) 267.
- [3] Y.S. Tsuo, Y. Xiao, C.A. Moore, in: Z.C. Feng, R. Tsu (Eds.), *Porous Silicon*, World Scientific, Singapore, 1994, p. 347.
- [4] A. Uhler, *Bell Syst. Tech. J.* 35 (1956) 333.
- [5] D.R. Turner, *J. Electrochem. Soc.* 105 (1958) 402.
- [6] S. Shih, C. Tsai, K.-H. Li, H.H. Jung, J.C. Campbell, D.L. Kwong, *Appl. Phys. Lett.* 60 (1992) 633.
- [7] R. Guerrero-Lemus, J.D. Moreno, J.M. Martinez-Duart, J.L. Corral, *Rev. Sci. Instrum.* 67 (1996) 3627.
- [8] D.C. Diaz, M. Osmanski, H. Guan, B. Das, *Rev. Sci. Instrum.* 64 (1993) 507.
- [9] K. Grigoros, V. Pacebutas, *Rev. Sci. Instrum.* 67 (1996) 2337.
- [10] R.W. Fathauer, T. George, A. Ksendzov, R.P. Vasquez, *Appl. Phys. Lett.* 60 (1992) 995.
- [11] L.A. Jones, G.M. Taylor, F.-X. Wei, D.F. Thomas, *Prog. Surf. Sci.* 50 (1995) 283.
- [12] Q. Chen, J. Zhu, G. Zhou, Z.T. Song, X-G. Li, Y. Zhang, *J. Phys. Condens. Mater.* 8 (1993) L753.

- [13] G. Amato, N. Brunetto, *Mater. Lett.* 26 (1996) 295.
- [14] U. Gosele, V. Lehmann, in: Z.C. Feng, R. Tsu (Eds.), *Porous Silicon*, World Scientific, Singapore, 1994, p. 17.
- [15] S.D. Campbell, L.A. Jones, E. Nakamichi, F.-X. Wei, L.D. Zajchowski, D.F. Thomas, *J. Vac. Sci. Technol. B* 15 (1995) 1184.
- [16] M. Enachescu, E. Hartmann, A. Kux, F. Kochi, *J. Luminescence* 57 (1993) 191.
- [17] H. Yamanaka, M. Kamoshida, Y. Haneta, *Jpn. J. Appl. Phys.* 13 (1974) 1661.
- [18] T.E. Bell, P.T.J. Gennissen, D. DeMunter, M. Kuhl, *J. Micromech. Microeng.* 6 (1996) 361.
- [19] W. Lang, P. Steiner, H. Sandmaier, *Sens. Actuators A* 51 (1995) 31.
- [20] Q.-S. Li, R.-C. Fang, in: Z.C. Feng, R. Tsu (Eds.), *Porous Silicon*, World Scientific, Singapore, 1994, p. 235.