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LETTER TO THE EDITOR**Atomically resolved structure of vacuum-heated porous silicon**

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Abstract. We report atomic resolution in scanning tunneling microscopy studies of porous silicon surfaces, after vacuum heat treatment at 850 °C and above. The (100) sample surfaces show some 2×1 reconstruction as for single-crystal (100) surfaces, but the (111) samples do not show any clear reconstructions, probably because the column tops are too small for large structures such as 7×7 to form. The atomic planes on the column tops are parallel to the substrate for both (100) and (111) samples, in agreement with low-energy electron diffraction studies.

It is usually difficult to obtain high-resolution scanning tunneling microscopy (STM) images of porous silicon (PS) surfaces, due in part to the high resistivity of the hydrided silicon surface, and also the uneven topography. Many STM studies have been published [1–15], but we are not aware of any that show clear atomic resolution. A representative display from a PS surface is shown in figure 1. The porous nature is evident, but atomic details are not obtained. In the case of scanning electron microscopy (SEM), clear high resolution images (10^5 magnification and more) are also difficult to obtain. We showed some time ago [16] that heat treatment of the material in vacuum at 250 °C has a marked effect in improving the sharpness of SEM images.

In further recent studies, it was found possible to obtain moderate-quality low-energy electron diffraction (LEED) displays from (100) and (111) PS surfaces if the samples were heated in ultra high vacuum (uhv) to around 850 °C for (100) samples and 950 °C for (111) samples [17]. The (100) samples showed 2×1 reconstruction, characteristic of clean (100) Si surfaces, but in the (111) surface patterns, fractional order LEED beams appeared only as streaks. The results showed that the underlying crystalline lattice extended to the very tops of the surface with areas sufficient to enable LEED patterns to form. The heat treatment used would have removed hydrides and also enabled the surface order, if damaged by the surface bond breaking, to reform (discussed below).

With the above knowledge, it was thought that STM displays with atomic resolution should be obtainable on vacuum heated PS surfaces, and such results are described in this report.

Three different types of Si wafer were used in this work, namely n-type (111) of resistivity 0.005–0.020 Ohm cm, n-type (100) 2–4 Ohm cm and p-type (100) 8–10 Ohm cm. The width of a sample was 10 mm, the length 10 mm and thickness 0.5 mm. The orientations were confirmed by observing etch pits with high-resolution optical microscopy.

An electrode was attached to a cleaned Si wafer by silver paste to form the ohmic back contact, which was then sealed with wax to prevent attack from the hydrofluoric acid electrolyte used for anodization. The counter electrode was a parallel platinum plate of area 1 cm^2 ,



Figure 1. STM image (19.5×19.5 nm) of 2–4 Ohm cm n-type (100) porous silicon surface in vacuum before heating. Constant current mode, tip voltage +1.28 V, current 1.12 nA.

positioned at a distance of about 1 cm from the wafer. The electrodes were held vertically in the electrochemical cell.

Anodization was carried out at 3 mA cm^{-2} current density for 7 minutes, in a magnetically stirred 1% aqueous HF solution [18]. In order to provide sufficient electrons in the case of n-type Si, those samples were illuminated with a 100 W tungsten light source from a distance of 10 cm at an angle close to normal.

Immediately after anodization, a sample was washed in a weak jet of ethanol for several seconds and dried by a stream of air. Such drying is not optimum for avoiding drying damage, but was used, together with the above anodization procedures, in order to compare results for samples previously used for devices [19]. Thereafter, the wax on the back of a sample was mechanically removed with care, and the PS layer was checked for uniformity both visually and by its photoluminescence (PL) under a UV lamp. It was then clamped on a quartz holder in a Burleigh ARIS 4400 uhv STM system. The total time of exposure to air was about 20 minutes. The system was evacuated until the pressure was lower than 9×10^{-9} Torr. It was not baked in order to avoid possible effects of water vapour desorbed from the system walls on the hot samples.

A sample was heated by slowly increasing current through it while maintaining a pressure in the low 10^{-7} Torr range. Heating was performed in stages to a temperature of around 850°C for (100) samples and 950°C for (111) samples for 30 minute periods. The samples were then cooled to room temperature for taking STM images. The STM tips were Pt-Ir alloy wires, electrochemically etched.

Sample temperatures were measured by two optical pyrometers, Mirage MR-6015, temperature ranges $250\text{--}600^\circ\text{C}$, and Leeds & Northrup, temperature ranges $750\text{--}2800^\circ\text{C}$. The pyrometers were calibrated against a thin contacting K-type thermocouple. The emissivity settings of the pyrometers were fixed at 1.0 during calibration and application.

The STM system allowed both sample and tip to be changed in vacuum if necessary. STM surface imaging was generally conducted in the constant height mode to optimize the topographic displays, and a given scan voltage was not varied during scans in order to avoid changing the conditions. Smoothing of the scan images using plane removal and Wiener noise filtering was usually applied to the raw data.

Clear atomic resolution surface structures were observable after the heat treatments described above. Representative scans are shown in figures 2 and 3. In figure 2 a scan of a p-type (100) surface is displayed, revealing 2×1 reconstruction (see caption). There was no discernible effect of conductivity type. The regions of ordered surface are clearly parallel to the substrate, as deduced from the LEED data [17]. The areas with clear atomic rows are fairly small, but larger areas of clear (100) 2×1 structure were not found in about 50 random placements of the STM tip. The scans show evidence of some atomic disorder and rather few adatoms and vacancies. The profile scans give data about atom spacings, which are consistent with the (100) surface [20]. Although clear 2×1 reconstruction was observed in some areas, we could not conclude that all patches showed regular reconstruction.

Figure 3 shows a typical (111) surface scan, displaying atomic resolution but no clear reconstruction. The angle between lines A–A and B–B is very close to 60° , as expected. In general, adatoms and vacancies were not in high concentration, but surface disorder seemed to be prevalent. One should note that STM can only sample a small proportion of any surface. However, based on many random tip placements, we formed the impression that STM scans from (111) surfaces showed somewhat fewer areas of atomic resolution than did (100) surfaces. The ordered regions were usually only a few nm in extent, which would account for the fact that the LEED patterns [17] in all cases displayed significantly poorer sharpness than from (100) and (111) single-crystal surfaces.

It is of interest that although many of the observed small (100) areas did show a reconstruction, the small (111) areas did not appear to possess regular reconstruction. This may be because the expected 7×7 reconstruction on the latter is too large to form on restricted (111) areas, whereas the 2×1 reconstruction is simpler in nature and readily fits on a small area. Surface strains on the porous surface structure may also play a role.

It is necessary to consider changes to the PS that may have been induced by the vacuum heat treatment. It has been reported [21] that heating PS in vacuum for 3 minutes at each of various raised temperatures causes surface hydrogen to evolve, with no further evolution after about 600°C . The visible PL shifts to the red, and eventually disappears after vacuum heating to about 420°C . After about 550°C , the band edges, which were shifted in the PS, revert to bulk Si values [21]. It has also been reported that SiH dissociates at about 460°C [22]. In earlier work, it was shown that hydrogen from SiH₂ species on PS surfaces desorbs on vacuum heating between about 370 and 430°C , whereas hydrogen from the SiH species desorbs between 450 and 530°C [23]. It has also been reported that hydrogen surface content on PS is almost completely removed on heating to 650°C [24].

Much LEED work has been previously carried out on Si single-crystal surfaces etched and cleaned by high-temperature vacuum heating. Temperatures at around 900°C and higher are sufficient to remove surface contamination and allow surface atomic reconstructions to form. Although most cleaning treatments feature flashing to about 1200°C for several seconds, it is possible, after argon ion bombardment, to heat at only 920°C for about 30 minutes and obtain good LEED patterns and atomic STM pictures [25]. We deduce from the above findings that in our experiments, the heat treatment we used would have removed all, or close to all, surface hydrogen, and annealed out any damage from the bond breaking. It also allowed reconstruction on the (100) surfaces, but was not hot enough to cause any major reformation of the surface regions. (The Si melting point is 1420°C .)

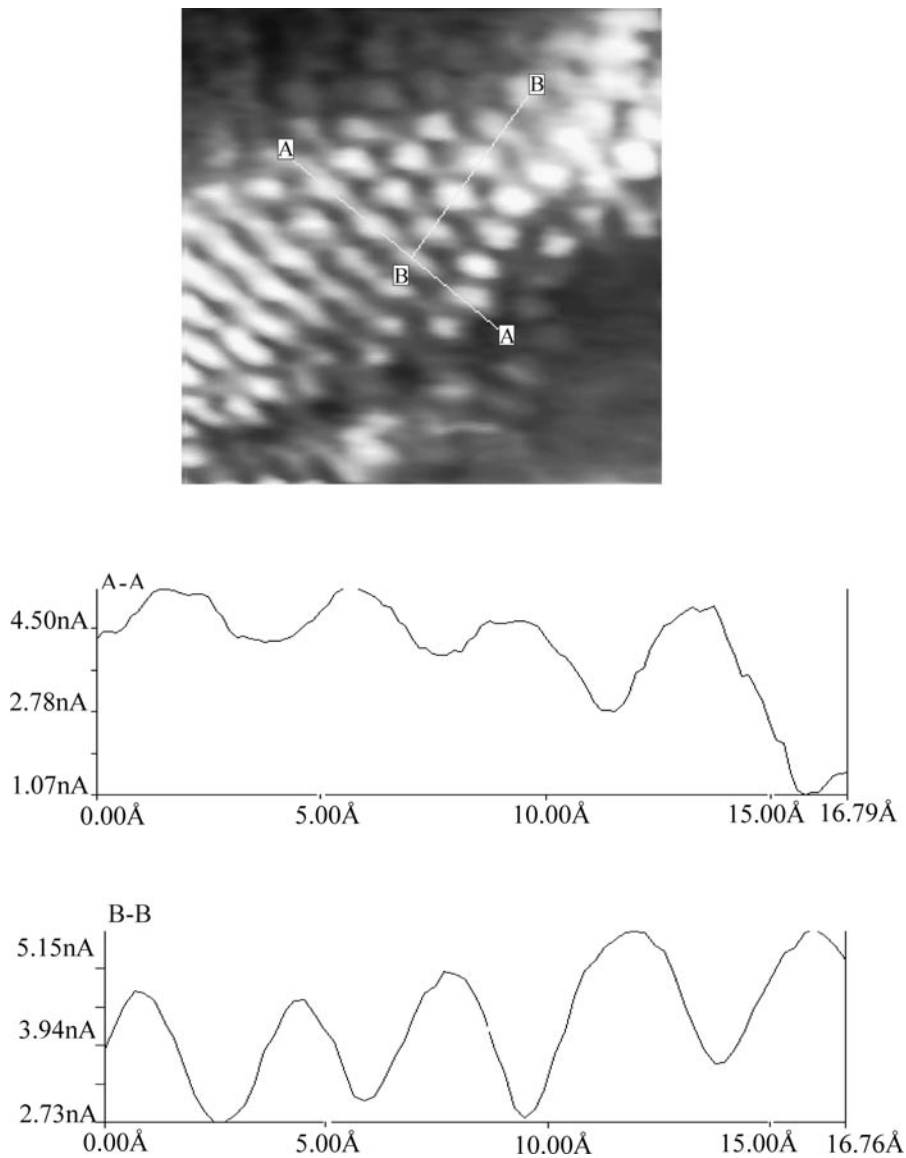


Figure 2. STM images in constant height mode, of (100) PS p-type, 8–10 Ohm cm sample after vacuum heating to 850 °C. Scan size 3.9×3.9 nm, tip voltage -0.07 V. Profile scans along the indicated lines A–A and B–B are also shown. The length scale was calibrated from a graphite surface. For the four peaks shown in the profile scan along the line A–A, the spacing between the first and second, and third and fourth, is 0.41 nm, with 0.35 nm between the second and third peaks, showing the pairing effect that constitutes a 2×1 reconstruction. Similar scans showing a 2×1 reconstruction are obtained on other spots and on n-type (100) samples. The average peak spacing along the scan line B–B is 0.38 nm, compared with a theoretical 0.384 nm. The angle between the lines A–A and B–B is close to 90° , being slightly affected by thermal drift.

The fact that (111) surfaces generally needed somewhat higher heating than (100) surfaces to develop clear atomic resolution may be connected to the fact that during anodization, pore (and hence column) growth is favoured along [100] directions, so that there are more strains

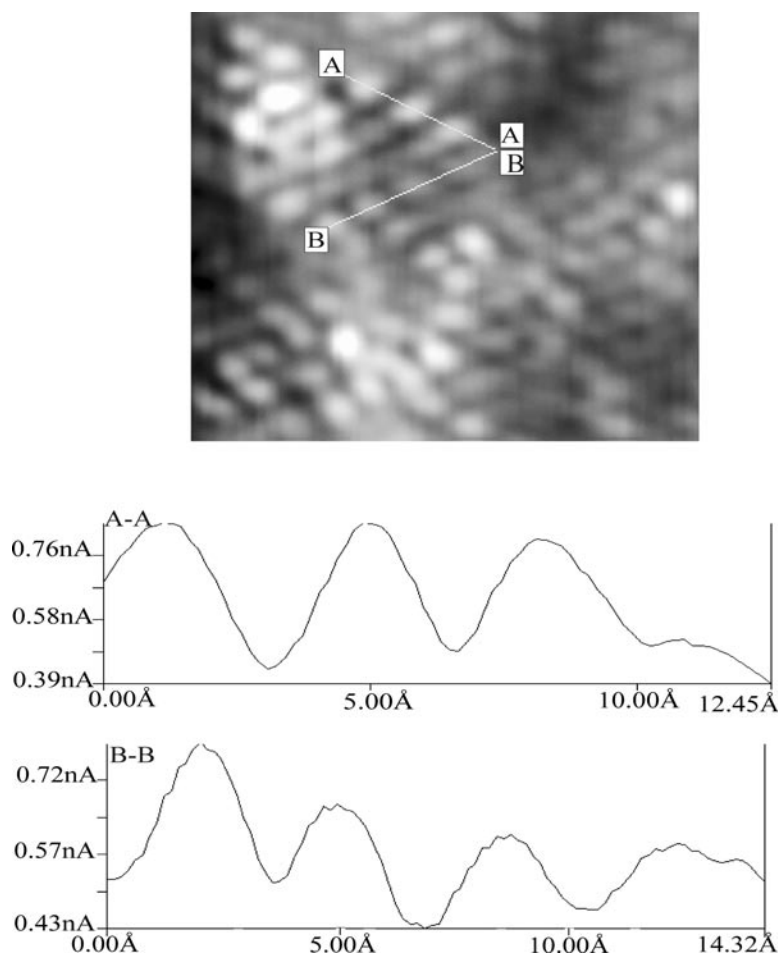


Figure 3. STM image, 3.5×3.5 nm, in constant height mode, of (111) PS sample, 0.005–0.02 Ohm cm n-type, after vacuum heating to 950°C . Tip voltage -0.06 V. Angle marked is close to 60° . Average distance between peaks on the profile scans A–A and B–B is 0.384 nm, as expected theoretically.

present in the (111) column tops. We noted that additional periods of heating in all cases seemed to have little further effect on the resulting STM displays.

In conclusion, we have found that PS surfaces heated in uhv to 850°C for (100) samples and 950°C for (111) samples, show small atomically ordered patches parallel to the original substrate. The (100) surface regions show 2×1 reconstruction, but the (111) surfaces do not show clear reconstructions, probably because the ordered patches are too small to allow large cells such as 7×7 to form readily.

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References

- [1] Laiho R, Pavlov A and Pavlova Y 1997 *Thin Solid Films* **297** 138
- [2] Gomez-Rodriguez J M, Baro A M and Parkhutik V P 1990 *Appl. Surf. Sci.* **44** 185

- [3] Enachescu M, Hartmann E and Koch F 1994 *Appl. Phys. Lett.* **64** 1365
- [4] Pavlov A and Pavlova Y 1997 *Thin Solid Films* **297** 132
- [5] Amato G 1995 *Japan. J. Appl. Phys.* **34** 1716
- [6] Enachescu M, Hartmann E, Kux A and Koch F 1993 *J. Lumin.* **57** 191
- [7] Mauckner G, Walter T, Baier T, Thonke K, Sauer R, Houbertz R, Memmert U and Behm R 1993 *J. Lumin.* **57** 211
- [8] Gu M, Syrykh C, Halimaoui A, Dumas Ph and Salvan F 1993 *J. Lumin.* **57** 315
- [9] Dneprovskii V, Eev A, Gushina N, Okorokov D, Panov V, Karavanskii V, Maslov A, Sokolov V and Dovidenko E 1995 *Phys. Status Solidi b* **188** 297
- [10] Parkhutik V P, Albella J M, Martinez-Duart J M, Gomez-Rodriguez J M, Baro A M and Shershulsky V I 1993 *Appl. Phys. Lett.* **62** 366
- [11] Chang S S, Yoon S O, Choi G J, Kawakami Y, Kurokawa S and Sakai A 1998 *Japan. J. Appl. Phys.* **37** 297
- [12] Dumas Ph, Gu M, Syrykh C, Hallimaoui A, Salvan E, Gimzewski J K and Schlittler R R 1994 *J. Vac. Sci. Technol. B* **12** 2064
- [13] Dumas Ph, Gu M, Syrykh C, Hallimaoui A, Salvan F and Gimzewski J K 1994 *J. Vac. Sci. Technol. B* **12** 2067
- [14] Dumas Ph, Gu M, Syrykh C, Gimzewski J K, Makarenko I, Hallimaoui A and Salvan F 1993 *Europhys. Lett.* **23** 197
- [15] Amisola G B, Behrensmeier R, Galligan J M, Otter F A, Namavar E and Kalkoran N M 1993 *J. Vac. Sci. Technol. B* **11** 1788
- [16] Sabet-Dariani R and Haneman D 1994 *J. Appl. Phys.* **76** 1346
- [17] Li W, Zhao D and Haneman D *Surf. Sci.* in press
- [18] Bertoletti M, Carasitti F, Fazio E, Ferrari A, La Monica S, Lazarouk S, Liakhov G, Maiello G, Proverbio E and Schirone L 1995 *Thin Solid Films* **253** 152
- [19] Kuznetsov V A, Andrienko I and Haneman D 1998 *Appl. Phys. Lett.* **72** 3323
- [20] Hamers R J, Avouris Ph and Bozso F 1987 *Phys. Rev. Lett.* **59** 2071
- [21] Van Buuren T, Tiedje T, Patitsas S N and Weydanz W 1994 *Phys. Rev. B* **50** 2719
- [22] Tvardauskas H, Bukauskaite B, Jasutis V, Leskiskas D and Simkiene I 1994 *Semicond. Sci. Technol.* **9** 1633
- [23] Gupta P, Colvin V L and George S M 1988 *Phys. Rev. B* **37** 8234
- [24] Cooke D W, Bennett B L, Farnum E H, Hults W L, Sickafus K E, Smith J F, Smith J L, Taylor T N, Tiwari P and Portis A M 1996 *Appl. Phys. Lett.* **68** 1663
- [25] Pashley M D, Haberen K W and Friday W 1988 *J. Vac. Sci. Technol. A* **6** 488