Direct evidence for the amorphous silicon phase in visible photoluminescent porous silicon

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We report on micro-Raman spectroscopy studies of porous silicon which show an amorphous silicon Raman line at 480 R cm^{-1} from regions that emit visible photoluminescence. A Raman line corresponding to microcrystalline silicon at 510 R cm^{-1} is also observed. X-ray photoelectron spectroscopy data is presented which shows a high silicon-dioxide content in porous silicon consistent with an amorphous silicon phase.

Recent reports[1] on the visible photoluminescence (PL) of porous silicon (PS) at room temperature have triggered much discussion on possible mechanisms for this phenomenon[2] and created the possibility of optoelectronic applications.[3] The observed phenomenon cannot be explained in terms of bulk silicon properties since the indirect band gap of silicon is in the near infrared. One recently proposed explanation is based on the assumption that high-porosity silicon can be considered to be a network of nanometer-size crystalline wires, and that quantum confinement effects in these one-dimensional structures are responsible for the widening of the band gap.[1] Earlier reports that the observed effect could be caused by hydrogen and/or oxygen atoms incorporated in an amorphous silicon (*a*-Si) matrix[4] were not considered due to the lack of direct evidence for the existence of the *a*-Si phase.[1] In this letter, we present, for the first time, direct evidence for the *a*-Si phase in PS based on micro-Raman spectroscopy.

The PS samples were made from *p*-type, boron-doped, (100) crystalline silicon (*c*-Si) wafers with a resistivity of 10–20 Ω cm, similar in resistivity to the *p* substrates used in Ref. 1. Silver was painted on the back of the wafers to produce a uniform potential and etching current on the front surface. The front surface was placed in a 40%–50% HF acid solution and electrochemically etched using constant current densities in the range 10–50 mA/cm^2. Typical etching times were 10–15 min. The etched surface was studied using scanning electron microscopy and scanning tunneling microscopy and was found to have a morphology consisting of a random array of small circular pores. This type of morphology is typically observed when using lightly doped *p* substrates.[5] The PS samples emitted bright red to yellow PL visible to the naked eye when excited by the 514.5-nm line of an argon laser or ultraviolet light.

Room-temperature Raman and PL measurements were performed using a micro-Raman system in which the laser spot size could be focused to 1 μm in diameter and positioned on the sample under an optical microscope. The advantage of microsampling is the ability to probe small sample regions having uniform morphological characteristics. The micro-Raman system consists of an Instruments-SA 1 m U1000 double monochromator coupled to an Olympus microscope with 50× and 100× objectives and a GaAs photomultiplier tube detection system. The excitation source was the 514.5-nm line of an argon ion laser. The typical laser spot size was approximately 20 μm in diameter with a power of 1 mW at the sample to avoid sample heating. The probe beam was placed on areas which were nominally flat so that the beam was uniform in extent. The Raman scattering on (100) *c*-Si was performed in the polarization geometry of $x(y,z)x$. To insure the accuracy of the Raman-phonon features, Raman measurements of high-purity *c*-Si were made for comparison after each run.

Figure 1 shows a micro-Raman spectrum from a photoluminescent region of PS made as described above. The background in spectrum A is due to the visible PL from the PS. Spectrum B shows the data after background subtraction. We observe a Raman line with the peak at 478 ± 2 R cm^{-1} and a full-width at half-maximum (FWHM) of 107 ± 1 R cm^{-1}, as determined by a best fit to a Lorentzian profile using a Nelder–Mead version of a sequential simplex optimization procedure. The Raman line at 478 R cm^{-1} corresponds exactly in position and width to the Raman line of *a*-Si.[6,7] We also observed the Raman line of *c*-Si at 521 ± 2 R cm^{-1} with a FWHM of 2.7 ± 1 R cm^{-1}, which may be originating from the Si substrate. The region of the sample shown in Fig. 1 showed mostly the Raman line of *a*-Si with no measurable Raman line of microcrystalline silicon. Other photoluminescent regions of the same sample showed, together with the Raman line of *a*-Si at 478 R cm^{-1}, the Raman line of microcrystalline silicon at 510 R cm^{-1}, as shown in Fig. 2. The best fit to the data in Fig. 2 using the simplex optimization procedure is two Lorentzian profiles centered at 479 ± 2 R cm^{-1} with a FWHM of 43 ± 1 R cm^{-1}, and 510 ± 2 R cm^{-1} with a FWHM of 24 ± 1 R cm^{-1}. The two-feature Raman spectrum of Fig. 2 is similar to the Raman spectrum reported for *a*-Si[7–9] and is attributed to a mixed phase of *a*-Si (480 R cm^{-1}) and microcrystalline silicon (510 R cm^{-1}).[9] The Raman line of microcrystalline silicon at 510 R cm^{-1} is

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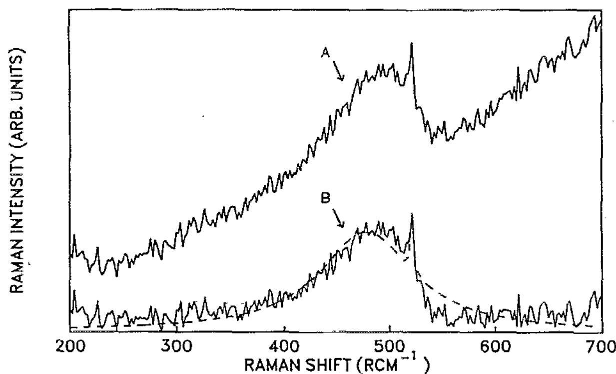

FIG. 1. Micro-Raman spectra from porous silicon. Spectrum A shows the raw data. Spectrum B shows the data after background subtraction. The dashed lines show the best fit to two Lorentzian profiles. The peaks determined by the fit are at 478 ± 2 R cm^{-1} (amorphous silicon) and 521 ± 2 R cm^{-1} (crystalline silicon).

due to TO phonons confined in microcrystals measuring several hundred angstroms in diameter.[9] The visible PL from the PS regions shown in Fig. 1 and Fig. 2 was similar, and is shown in Fig. 3 for the region shown in Fig. 2. Thus, visible PL is emitted from PS regions that have both amorphous and microcrystalline components. All PS regions that emitted visible PL showed the Raman line of a-Si, and, as shown in Fig. 1, visible PL was emitted from PS regions that showed mostly the Raman line of a-Si. The possibility that the visible PL from PS may be due to confinement in silicon microcrystals cannot be excluded. However, the a-Si phase should also be considered as a possible mechanism since the a-Si phase was present in all photoluminescent PS regions. Similar results showing an a-Si phase in visible photoluminescent PS were obtained from all PS samples obtained from other suppliers.

Recently, Tsu, Shen, and Dutta[10] reported that PS which emitted visible PL did not show the Raman line of a-Si at 480 R cm^{-1} and only showed the Raman line of microcrystalline silicon at 511 R cm^{-1}. It should be pointed out that their study used macro-Raman sampling techniques, and the 511 R cm^{-1} Raman line they observed can be attributed to microcrystalline Si in a mixed phase of

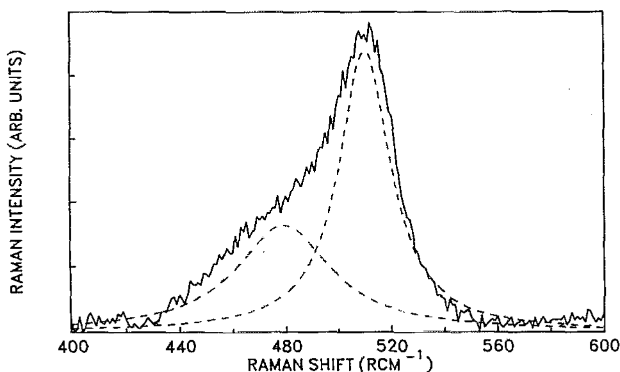

FIG. 2. Micro-Raman spectrum from a different sample region showing amorphous and microcrystalline silicon contributions. The dashed lines show the best fit to two Lorentzian profiles. The peaks are at 479 ± 2 and 510 ± 2 R cm^{-1} (TO phonon line of microcrystalline silicon).

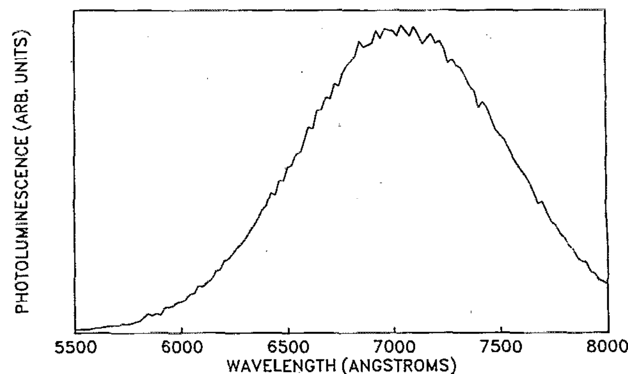

FIG. 3. Photoluminescence spectrum from the region of Fig. 2.

microcrystalline and amorphous silicon,[7–9] as we have described.

The possibility that visible PL from PS could be due to hydrogen and/or oxygen atoms incorporated in an a-Si phase was first suggested in Ref. 4, based indirectly on the similarity between the PL spectra from PS and hydrogenated amorphous silicon (a-Si:H). Wolford *et al.*[11] reported efficient visible PL from a-Si:H, and attributed the PL to the formation of (SiH_2) polysilane chains in a-Si. A similar mechanism may apply to the a-Si phase in PS since the surface of PS has been reported to be saturated with SiH_2 bonds.[12] More recent reports have shown that a sharp drop in the visible PL intensity of PS occurs when the surface SiH_2 species is desorbed at temperatures greater than 300 °C.[13] Oxygen incorporation in a-SiO_x:H has also been reported to shift the PL peak of a-Si to energies in the visible spectrum.[14] To determine the SiO_2 content on the surface of the PS samples, we analyzed the samples using x-ray photoelectron spectroscopy (XPS) at a base pressure of 1×10^{-9} Torr using a Perkin-Elmer 5100 with a hemispherical analyzer. A detailed scan of the silicon $2p$ region, shown in Fig. 4, showed a high Si^{+4} intensity from SiO_2 compared to Si^0.[15] The spectrum is shifted due to sample charging (SiO_2 being an insulator). Although the XPS data may be interpreted as being due to a SiO_2 layer on top of the amorphous and microcrystalline Si, the data do not rule out the possibility of an a-SiO_x:H phase being present.

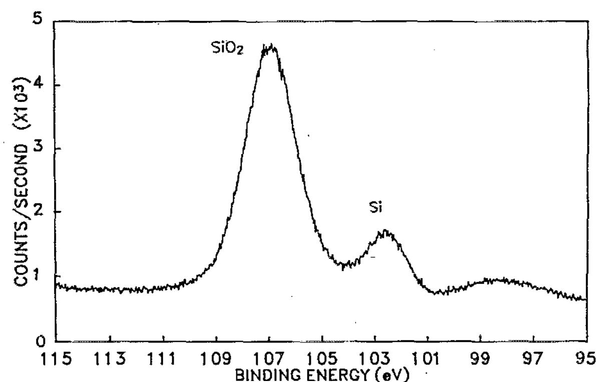

FIG. 4. X-ray photoelectron spectroscopy spectrum of the silicon $2p$ region from porous silicon. The spectrum is shifted by approximately 4 eV to higher binding energy due to sample charging.

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In conclusion, we have presented direct evidence based on micro-Raman spectroscopy for the *a*-Si phase in PS which emits visible PL. This finding supports a mechanism for visible PL from PS based on *a*-Si such as hydrogen and/or oxygen incorporation in *a*-Si.

Note added in proof: After submission of this letter, Vasquez, Fathauer, George, Ksendzov, and Lin[16] published a paper reporting evidence for the amorphous phase in visible photoluminescent porous silicon based on XPS data. Our independent results are consistent with this work and we are grateful to the referee for bringing this work to our attention.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] See for example, the special session on porous silicon at the Materials Research Society, 1991 Fall Meeting, December 6–13, 1991.

[3] A. Halimaoui, C. Oules, G. Bomchil, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, and F. Muller, Appl. Phys. Lett. **59**, 304 (1991).

[4] C. Pickering, M. I. J. Beale, D. J. Robbins, P. J. Pearson, and R. Greef, J. Phys. C **17**, 6535 (1984).

[5] G. Bomchil, A. Halimaoui, and R. Herino, Microelectron. Eng. **8**, 293 (1988).

[6] G. S. Oehrlein, R. M. Tromp. J. C. Tsang, Y. H. Lee, and E. J. Petrillo, J. Electrochem. Soc. **132**, 1441 (1985).

[7] D. J. Olego and H. Baumgart, J. Appl. Phys. **63**, 2669 (1987).

[8] F. H. Pollack and R. Tsu, SPIE **452**, 26 (1983).

[9] E. Bustarret, M. A. Hachicha, and M. Brunel, Appl. Phys. Lett. **52**, 1675 (1988).

[10] R. Tsu, H. Shen, and M. Dutta, Appl. Phys. Lett. **60**, 112 (1992).

[11] D. J. Wolford, B. A. Scott, J. A. Reimer, and J. A. Bradley, Physica B **117**, 920 (1983).

[12] A. Venkateswara Rao, F. Ozanam, and J.-N. Chazalviel, J. Electrochem. Soc. **138**, 153 (1991).

[13] C. Tsai, K.-H. Li, J. Sarathy, S. Shih, J. C. Campbell, B. K. Hance, and J. M. White, Appl. Phys. Lett. **59**, 2814 (1991).

[14] R. Carius, R. Fischer, E. Holzenkampfer, and J. Stuke, J. Appl. Phys. **52**, 4241 (1981).

[15] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prarie, MN, 1979).

[16] R. P. Vasquez, R. W. Fathauer, T. George, A. Ksendzov, and T. L. Lin, Appl. Phys. Lett. **60**, 1004 (1992).

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