Journal of Porous Materials 7, 381–383 (2000)

Effect of Light Exposure and Ultrasound on the Formation of Porous Silicon

S. KALEM, O. YAVUZCETIN AND C. ALTINELLER
TUBITAK, Institute of Electronics, P.O. Box 21, Gebze 41470, Kocaeli, Turkey

Abstract. We have investigated the effect of light exposure and ultrasonic (US) treatment on the formation of porous Si layers grown by electroless stain-etching technique. It was shown that; the He-Ne laser exposure resulted in a considerable increase in both the hydrogenation and the oxidation amounts in n-type Si, but a decrease in p-type wafers. The effect is attributable to effective change in the concentration of free hole carriers. The UV light exposure has led to the shift at the peak positions, indicating probably a change in bonding configuration, and increase in oxidation. Also, a correlation was established between the ultrasonic treatment and the microstructure. The US treated samples exhibit a decrease in hydrogenation and oxidation. UV exposure together with the US has led to a further decrease in both hydrogen and oxygen amounts, which was rather indicative of an excessive surface etching.

Keywords: porous silicon, microstructure, infrared spectroscopy

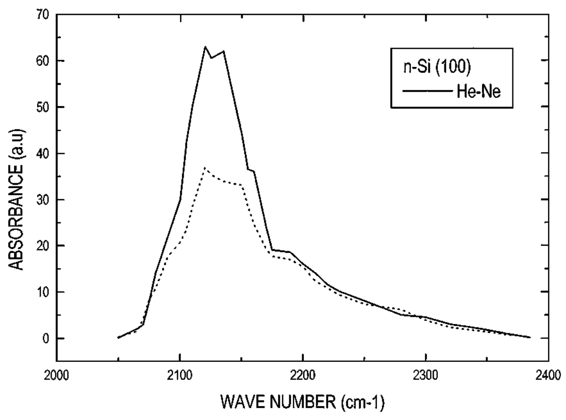
Porous semiconductors have been known for sometime, offering promising applications in the field of optoelectronics [1, 2]. Most of the efforts were concentrated on finding the ways leading to more stable and controllable material properties. The replacement of less stable hydrogen with more stable oxygen is for example one of the most challenging problems [3]. Hence, the control of material properties with external applications such as the light and ultrasound can be very important.

The objective of this work is to investigate the effect of light exposure and ultrasound (US) on the formation of porous semiconductors. The effect of light exposure on semiconductor processing has been known for sometime [4]. It was also shown that the UV exposure could play an important role in determining the size of micropores in porous semiconductor [5]. The US, on the other hand, can have similar effects such as the changes in density and crystal size through the process of sono cavitation [6]. There has already been successful applications using the US cavitation to the synthesis of materials [7]. Despite their importance, the current knowledge of the formation process associated with the light irradiation and the ultrasound is not well established. Therefore, there is a need of a systematic study to determine the role of these excitations in the formation of porous semiconductors.

In this work, we report on the optical and infrared vibrational properties of porous silicon layers grown on a variety of wafers by electroless etching technique under the effect of light exposure and ultrasonic treatment. We have carried out experiments in a systematic way in order to determine their effect on the formation of porous Si. In the experiments, both the n-type and the p-type Si wafers of different resistivities with both the (1 0 0) and (1 1 1) orientations were used. FTIR, photoluminescence (room temperature) and SEM (Scanning Electron Microscope) have been used for the subsequent analysis of the samples. The thickness of layers is about 0.3 micron as measured by SEM. The porous layer formation was done in 4 : 1 : 5 ($HF : HNO_3 : H_2O$) solution using the stain-etching technique.

Light Effect

A He-Ne laser of 5 mW was used as visible light source at 632.8 nm to irradiate samples during the porous layer formation. Figure 1(a) and (b) shows the spectra of Si—H and Si—O—Si stretching modes, respectively.



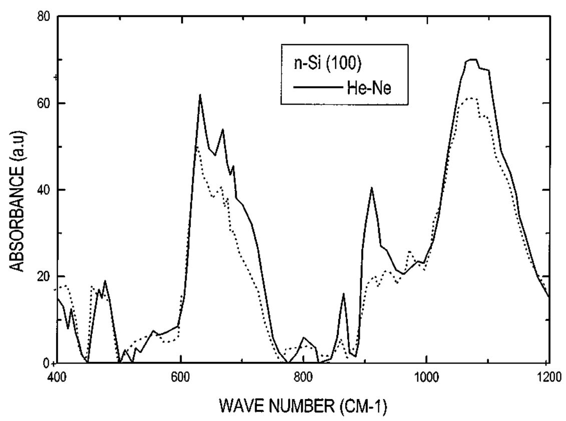


Figure 1. Effect of He-Ne exposure on anodication of (1 0 0) n-Si of 11 Ohm · cm resistivity. (a) Si—H stretching modes and (b) Si—O—Si str. and other Si—H bands. Dotted and solid lines represent the spectra from samples grown under dark and He-Ne illumination, respectively.

The layer was formed on an n-type (1 0 0) Si wafer of (11 ± 9) Ohm·cm resistivity, which was etched for 20 min. As evidenced from the FTIR spectra, the He-Ne laser exposure leads to a considerable increase in the amount of hydrogenation and oxidation. We attribute this effect to an increase in the concentration of free hole carriers, which are necessary elements for porous layer formation. From the PL measurements, we estimated an effective band gap corresponding to about 650 nm, indicating that the He-Ne laser can excite hole carriers. We also observe similar behavior on layers etched for longer duration, but with stronger increase in intensities of the relevant Si—O and Si—H vibrational bands. By analyzing IR band shapes, one can attribute the band intensities to an increase in thickness. However, the bands in He-Ne exposed samples are much narrower. For example, the band shape of Si—H stretching modes is more like a single mode vibration. Also, the relative increases in intensity of the modes at 900 cm^{-1} and at 865 cm^{-1} are considerable.

For p-type wafers, a decrease in oxygen and hydrogen incorporation or no considerable effect has been observed upon He-Ne laser illumination. These changes can be attributed to the recombination of charge, carriers that lead to an effective decrease in available hole concentration. In n-type samples, there are not very significant changes at the Si—O—Si band shapes. Thus, one can suggest that the band intensities are mostly related to different layer thickness.

The effect of UV light exposure on the formation of porous layers on p-type (1 0 0) Si with (5–10) Ohm · cm resistivities is shown in Fig. 2. We observe a slight increase in hydrogenation and oxidation as observed in IR through vibrational bands at around 2140, 630 and 1060 cm^{-1}. Note that the oxidation is much stronger than hydrogenation under UV. In addition, we observe an enhancement at the TO phonon mode at around 460 cm^{-1} as shown in Fig. 2. The UV light is a very well known agent for oxide growth in Si. The observation of this small effect can be related to an increase in surface temperature due to UV radiation heating. The UV light is a very effective tool for heating Si wafers. We know from the temperature dependent experiments that, the heating unfavors the porous layer formation. In some samples, for example n-type Si of low resistivity (0.015–0.060 Ohm · cm), the UV light exposure favored the formation of monohydrides. This is confirmed by the change at the peak positions of Si—H bands toward low energies. No spectra could

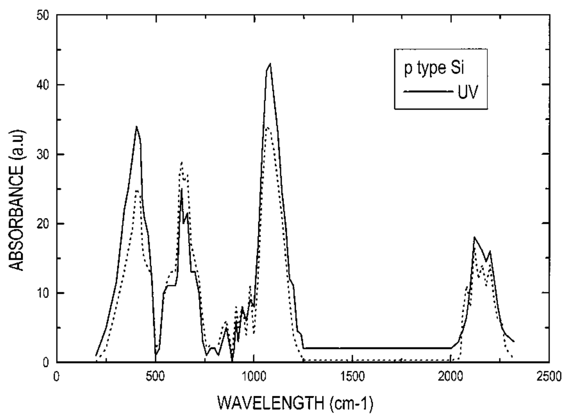


Figure 2. Effect of UV exposure on the formation of porous layer on (1 1 1) p-Si. Solid line represents the spectrum of the sample grown under UV light.

be recorded beyond 1360 cm^{-1}, probably due to low resistivity.

Ultrasonic Effect

US cavitation has been considered as a useful tool for cleaning and etching applications in microelectronics processing. In this work, we have shown that it can be used to induce useful microstructural changes in the porous layers. The ultrasonic treatment during layer formation resulted in the following microstructural features in p-type (1 0 0) Si (10 min of stain-etching): i) Change in bonding configuration, ii) decrease in oxidation and hydrogenation, and iii) Si—H band narrowing (Fig. 3). The decrease in Si—H and Si—O band intensities indicates probably that there is some etching activity induced by US cavitation. The reason for the Si—H band narrowing is attributable to the fact that US cavitation enables us to prepare structurally homogenous samples. Note that we have not observed any significant narrowing in Si—O—Si band at 1060 cm^{-1}. As shown in Fig. 3, there is a significant shift toward low energies at the stretching mode peak position at around 2200 cm^{-1}. A single vibrational mode at 2140 cm^{-1}, which is probably due Si—H vibration, dominates the spectrum in the sample treated with US.

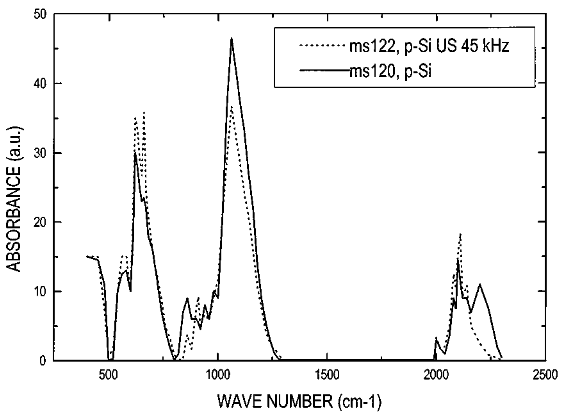


Figure 3. FTIR spectra showing the effect of US treatment. Dotted line represents the spectrum of the sample grown under US treatment.

This result indicates that the US cavitation favors the formation of monohydrides to the detriment of multihydride formation. The relative increase of hydrogenation compared to oxygen is also confirmed by the Si—H related vibration at around 630 cm^{-1}. The ratio of Si—H to Si—O—Si is much stronger in US cavitated sample as estimated from the relative band intensities. On the other hand, UV exposure combined with the US treatment has resulted in a considerable decrease in intensities of all the IR bands. In addition, this combination removed the features at the high frequency shoulders of the bands resulting in narrower Si—H bands. This band narrowing may be indicative of presence of some structural order. Therefore, it would be useful to determine the PL band shape as a function of US power.

In conclusion, we have shown that the He-Ne laser, US cavitation and UV light exposure have considerable effects on the porous layer formation. This effect has dependence on the type and resistivities of the wafers. The He-Ne laser exposure increases the growth rate of the porous layer. The US cavitation leads to porous layers with decreased oxidation and hydrogenation and to an affective etching when combined with UV light. The effect of US on photoluminescence properties is currently under investigation.

Acknowledgment

This work was supported by NATO-Scientific Affairs Division under CRG950830.

References

1. L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
2. V. Lehmann and U. Gosele, Appl. Phys. Lett. **58**, 856 (1991).
3. N. Rigakis et al., J. Appl. Phys. **81**, 440 (1997).
4. I.W. Boyd, in *Advances in Rapid Thermal and Integrated Processing*, edited by F. Roozeboom (Kluwer Academic Pub., 1996), p. 235.
5. V. Lehmann, J. Electrochem. Soc. **140**, 2836 (1993).
6. K.S. Suslick, MRS Bulletin **20**, 29 (1995).
7. R. Roy, J. Sol. St. Chem. **111**, 11 (1994).