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Structure of Porous Silicon Formed on n-Type Silicon Wafer

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Abstract

Porous silicon is one of attractive light-emitting materials nowadays. The advantage of silicon-related light emitting materials is an environmental-friendly property and low cost of the material. Light-emitting porous silicon has extensively been studied for more than twenty years, mainly being formed on a p-type silicon wafer. The n-type silicon is also of importance because the pn junction, made of the two types of silicon, is a key structure for electronic devices. This article reports the formation of porous silicon formed on n-type silicon wafers and shows the surface and cross-sectional structures observed by a scanning electron microscope. The formation characteristics of porous silicon on n-type silicon wafers are discussed.

Keywords

Porous Silicon, n-Type Silicon Wafer, Surface Structure, Scanning Electron Microscope

1. Introduction

Silicon is the most basic and indispensable material to semiconductor devices such as diodes, transistors and integrated circuits. Silicon is fortunately nontoxic and then harmless to human bodies at the same time. The abundance of this material can contribute to the low cost of device fabrications.

Silicon is not appropriate, on the other hand, for a material of light emitting devices because the efficiency of light emission is quite low based on the fact that silicon is an indirect transition semiconductor. This is why III-V group compound semiconductors such as GaP have been used to realize light emitting diodes. Lately, GaN has become popular to be a key material for blue light emitting diodes. The disadvantages of these compound semiconductors are mostly toxic and then harmful to human bodies. And so, the problem of the environmental load should be considered.

It is known before long that when silicon wafer is processed by means of fine electric current in HF acid solution, the surface is made into a porous structure. In 1990, L. T. Canham discovered that the porous silicon exhibits photoluminescence and showed the possibility of light emitting material [1]. Afterward vast amount of researches have been performed worldwide to develop a light emitting device with porous silicon [2].

The realization of light emitting devices with silicon is welcome from an environmental view. There is another advantage of silicon-based light emitting devices. Since widely used integrated circuits are made on silicon tips, an opt-electronic integration can be fabricated on one silicon tip together. It will open a new way to an opt-electronic integration scheme in the future.

The structure of porous silicon strongly depends on forming conditions during anodization; i.e. anodization time [3], current density [3], contents of solution [4], light irradiation [5], and so on. In addition, chemical [6] and heat [7] treatments also affect the structure strongly.

When forming porous silicon by means of anodization, p-type silicon wafers have been widely used as a starting material. It is because the formation of porous structure requires positive holes in silicon. When n-type silicon is used to form porous silicon, light irradiation should be accompanied during anodization for the creation of holes in silicon. It can be said that with p-type silicon wafers the formation of porous silicon can be performed in a rather simple way.

In this article, it has been challenged to investigate the structure of porous silicon with an n-type silicon wafer. Physical structures of the obtained porous silicon have been observed, and the formation mechanism is discussed. Photoacoustic spectroscopy of the obtained porous silicon has also been studied.

An n-type porous silicon has not been so much studied so far. Some researchers investigated x-ray rocking curve [8] and Raman spectra [9]. Further, an electroluminescence from a Schottky device composed of n-type porous silicon and Al showed a steady increase of light emission in 800 hours [10]. The device also showed a fast response at 200 MHz and the chromaticity diagram of the device was studied [11]. In addition, n-type porous silicon was also used to prepare a field emitter [12].

2. Experimental

In this experiment is used (111) n-type silicon wafers the resistivity of which was in the range of 1.7 to 10 Ω·cm. A (111) n-type silicon wafer has not been used as widely as a (100) wafer with a few exceptions [13]-[15]. The one side of the wafer was optically polished where porous structure was formed. Anodization was performed with a simple apparatus that consists of a container of HF acid-based solution in which a piece of silicon wafer and a counter electrode of Pt was installed. The solution (100 ml) consists of HF acid (50 wt.%): ethanol = 1:1 in volume [15] [16]. The area of anodization was 1.23 cm^2. The intentional irradiation of light was not engaged during the anodization.

Four kinds of samples are engaged in this paper. The three samples A, B and C were formed under the current density of 211 mA/cm^2. The anodization time for the three samples was 7.5, 15 and 30 minutes, respectively. The current density of the sample D was only as large as 106 mA/cm^2 for 30-minute anodization.

The surfaces and cross sections of the obtained porous silicon samples have been observed with a scanning electron microscope (SEM) of S-570 by Hitach Co. Ltd. at an acceleration voltage of 20 kV to the incident angle of 60 degree. A photoacoustic spectroscopic analysis was made with a self-made system equipped with 500 W Xenon lamp as an exciting light source at a chopping frequency of 40 Hz. The photoacoustic signal was detected by a condenser microphone in a conventional way. The whole system was controlled by a personal computer.

3. Results and Discussion

Figure 1 in the left shows SEM photograph of the surface and cross sectional view of Sample A. In this photo, the surface is shown in the upper side and the cross section in the lower. There are countless small dips on the surface and some linear patterns looking like trace of corrosion on the cross section. These marks hardly imply that porous silicon was formed. The top view of the surface is shown in the right side at the magnification of 3000. According to this photo, countless dips over the surface have the triangular form about 2 μm. All triangles are arranged in the same direction. From the fact that the silicon wafer had a (111) direction at the surface, this arrangement means that the reaction during anodization depends on the crystal orientation. It is interesting to point that when p-type silicon wafer is used circular holes are likely to be formed at the surface, not triangular. This indicates that the velocity of chemical reactions forming porous silicon is far smaller in n-type silicon wafers. Christophersen et al. reported [17] SEM photographs indicating square macropores. They used (100) n-type wafers with a low resistivity (0.02 to 0.06 Ω·cm) and anodized them without light irradiation. It can be understood in a similar sense. On the other hand, Kwon et al. showed irregular and complicated nanopore forms far from a square using (100) high-resistivity (5 to 12 Ω·cm) wafers [16]. They also showed photoluminescence spectra that showed a weak maximum structure at 700 nm when the anodization time was 20 s, and then the stronger structure at 570 nm when the anodization time increased to 3 min.

Next considered are the results of Sample B. The SEM photograph of the surface and the cross section of the sample are shown in the left of **Figure 2**. The cross sectional image tells us that the reaction proceeded to a great extent. The surface structure at the right side is different from that of the left side. It shows in the right part the surface layer was removed because there is a step between the right and left regions. This step is magnified to 1000 times in the center of **Figure 2**. In this photo, it is quite easy to recognize that the lower part is where the surface layer was removed end the complicated structure beneath the surface layer was exposed.

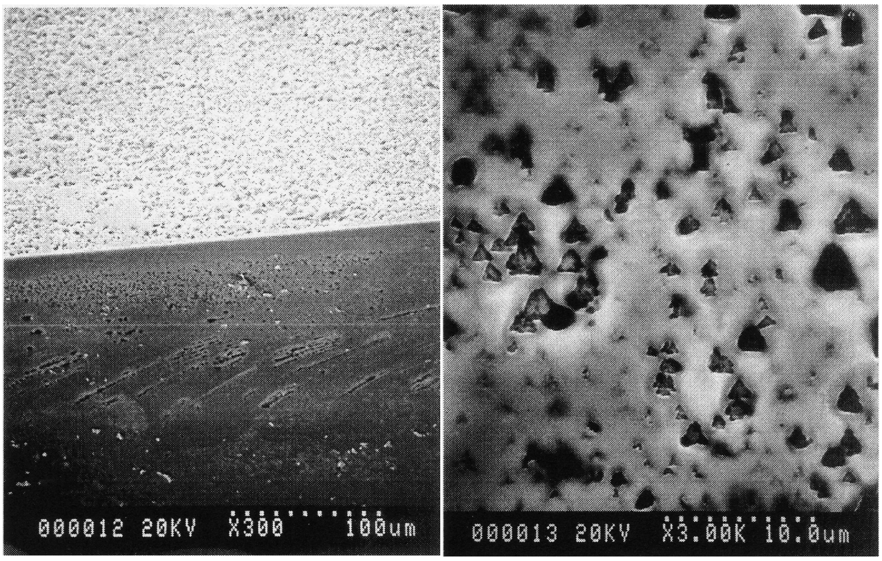

Figure 1. SEM photographs of Sample A; the surface and the cross section from the upper (right) and the enlarged of the surface (left).

The structure is quite rough and zoomed in on the surface in the left photo. Many triangular structures, big or small ones, are seen in the photo to be piled up but all in the same direction. Compared with the smooth surface of the upper part in central figure, the chemical reaction forming porous silicon proceeded to a formidably great extent under the surface layer. Another interest point is that the triangular dips are arranged along parallel straight lines on the surface layer as is apparently shown in the central figure. It is possibly because the strain induced by the mirror polishing of the surface promoted the chemical reaction to form porous silicon.

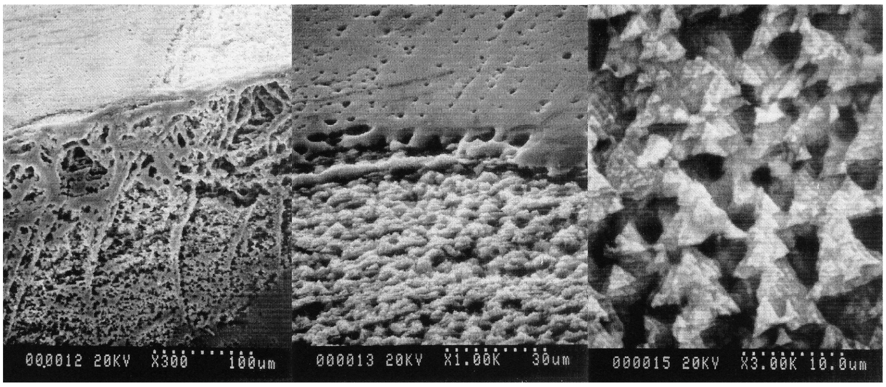

Figure 2. SEM photographs of Sample B; the surface and the cross section from the upper (right), the enlarged of the surface (center), and the enlarged at the complicated structure lower in the central figure (right).

Figure 3 in the left shows the SEM photograph of the surface and cross section of Sample C. The right photo shows the expanded SEM photograph of the surface. There are infinitely numerous microstructures spread over the surface. These structures are smaller than those in Sample B. From the cross sectional view, it looks like a granular state that can easily collapse.

Figure 4 in the left shows the photograph of the surface and cross section of sample D that was formed at a half current density of the other samples. The anodization time of 30 minutes is the same as sample C. Only in this case, a prominent structure is observed in a cross sectional area that many straight lines have grown in the direction at 45 degree to the surface. This interesting structure, which has not been observed in the other samples A, B and C, implies the dependence of the crystal lattice orientation. This can be elucidated by the slowness of the chemical reaction forming porous silicon inside the wafers. It is consistent with the slow formation of porous silicon that the number of positive holes is small in n-type silicon because positive holes are required for the chemical reaction. In Sample D, the current density was the half of the other samples, and then the supply of holes accordingly became the half that resulted in a slower reaction inside silicon wafers. The right photo shows the surface SEM photograph of Sample D from an angle of 45 degree. There are triangular holes that are apparently sparse compared with Sample C. The chemical reaction seems to proceed more conspicuously inside the wafers.

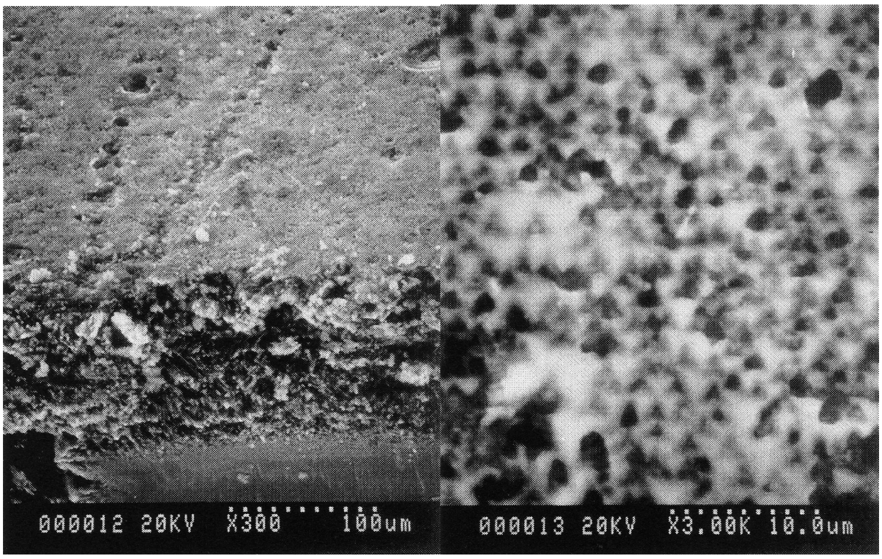

Figure 3. SEM photographs of Sample C; the surface and the cross section from the upper (right) and the enlarged of the surface (right).

A photoluminescence experiment was performed with excitation mercury lamp at 633 nm on all four kinds of samples but no photoluminescence was observed in any cases even though Kwon et al. observed photoluminescence from n-type porous silicon. It might be because the exciting light was not strong enough in this experiment. For example, Chen et al. used a He-Cd laser to excite porous silicon [15]. A photoacoustic spectroscopy (PAS) of Sample C was measured, that is shown in **Figure 5**. This figure shows that absorption, i.e. PAS amplitude, steeply increases with the photon energy under 1.6 eV and that it continues to increase above 1.6 eV even though it is not so steep. This spectrum is quite different from

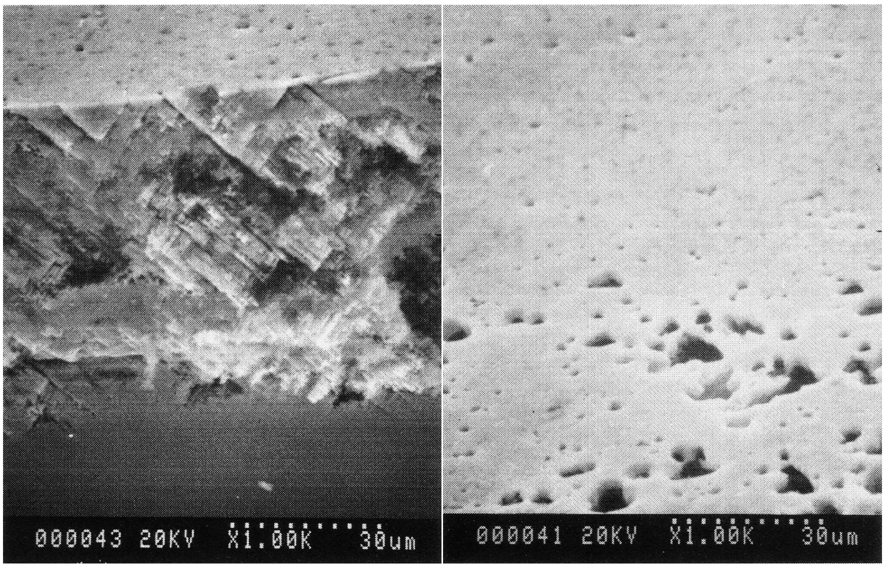

Figure 4. SEM photographs of Sample D; the surface and the cross section from the upper (right) and the surface (right).

that taken from p-type porous silicon samples. A luminescent p-type sample provides PAS amplitude that is constant from 1.1 to 1.6 eV and increases monotonically with photon energy above 1.6 eV. If the sample is not luminescent well, the PAS amplitude increases prominently with photon energy in the range between 1 and 2 eV. This phenomenon is well understood in such a way that noticeable absorption between 1 and 2 eV depresses light emission efficiency [18]. The next interesting point is the reason why the absorption becomes large in this region when porous silicon is formed on an n-type silicon wafer.

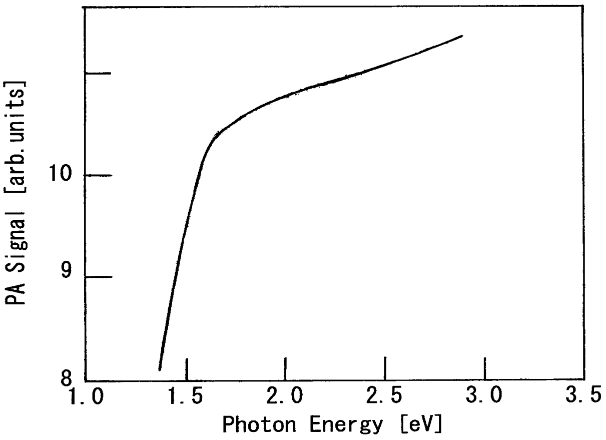

Figure 5. Photoacoustic spectrum of Sample C.

4. Conclusion

Porous silicon was formed on n-type silicon wafers and its surface and cross section features was studied by means of a scanning electron microscopy as well as photoacoustic spectroscopy. Various features in SEM photographs have been obtained depending on the forming conditions. It was found that the chemical reaction forming n-type porous silicon is quite slow compared with p-type silicon. The slowness of the reaction was suggested in the fact that corrosion shape depends on the crystal orientation both on the surface and inside the wafer. The chemical reaction forming porous silicon is noticeable to a greater extent inside wafers than at the surface. Photoluminescence was not observed from all samples. A PAS spectrum showed that a comparatively large absorption exists between 1 and 2 eV, which probably depress the light emitting efficiency as is reported in p-type porous silicon cases. The next interesting point is the reason for absorption and the difference of absorption characteristics between the surface and the inside of the porous silicon.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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