The dependence of hydrofluoric acid concentration during anodization on photoluminescence of porous silicon

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Abstract

The mixture of hydrofluoric (HF) acid and ethanol is used as an electrolyte during anodization of silicon. We investigated the effect of the ratio of HF acid to ethanol on photoluminescence. It is concluded that porous silicon anodized with the electrolyte containing 35 or 40% HF acid provides strong photoluminescence. The fact implies the existence of a chemical reaction including ethanol during anodization other than electrochemical reaction. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Light emitting porous silicon has attracted much attention since Canham [1] first reported the emission from porous silicon. It is plausible because crystalline silicon is an indirect semiconductor and has little efficiency in light emission. A number of studies have been devoted to light emitting porous silicon for 10 years. Light emitting diode of porous silicon has been progressed recently to a great extent [2].

A major interest is focused on the development of light emitting devices and revelation of the mechanism of light emission. While some researchers reported the evidence of a quantum effect [3,4], other experimental results, which could not be explained by the quantum effect, were also published [5]. Other than quantum effects, chemical effect is believed to be a reason for light emission [6]. The mechanism of light emission from porous silicon is controversial even today.

On the other hand, it is not yet well studied how the anodization conditions affect the luminescent properties. Ohmukai et al. reported that photoluminescent (PL) intensity depends on current density during anodization [7]. Recently, the influence of anodization conditions on photocconductivity spectra has been reported [8]. It is important to clarify the relation between anodization conditions and PL characteristics of porous silicon in the aspects of the fabrication of light emitting devices and the physical understanding of the emission. In this article, we concentrate on the dependence of HF acid concentration during anodization on PL spectra.

2. Experimental

Porous silicon was made up of a (100) p-type silicon wafer, whose resistivity was 1–10 Ω cm. Anodization was performed in an electrolyte (100 ml) consisting of ethanol and 50 wt% hydrofluoric (HF) acid. The ratio of the HF acid to ethanol was varied from 30 to 55%. The current density and anodization time were 20 mA/cm² and 3600 s, respectively. It was because previous work adopted the current density between 15 and 50 mA/cm² and the anodization time between 120 and 7200 s [9]. A Pt rod was used as a counter electrode. The anodized area was 2.54 cm². Illumination of the silicon wafer was not specifically performed during anodization.

Anodization was followed by chemical etching with a solution of HF/ethanol/water = 1:2:1 for 120 s for the enhancement of the PL efficiency. After chemical etching, the samples were rinsed with deionized water and then dried with nitrogen gas in order to minimize surface oxidation.

PL spectra were taken with exciting light at 376 nm (3.3 eV) from an ultraviolet lamp. PL emission was analyzed using a single monochromator and detected by a silicon photodiode. The exciting light was chopped at 80 Hz.
to apply a lock-in amplifier. The resolution of PL spectra was under 10 nm.

3. Results and discussion

Fig. 1 shows the PL spectra obtained from porous silicon in the variation of HF acid concentration. Each spectrum consists of one broad peak situated between 728 and 816 nm whose full width at half maximum is around 200 nm. Although the peak position of PL spectra cannot be explained systematically, all PL emissions are limited in the region between 600 and 1000 nm. The wavelength giving the maximum PL intensity in each structure has no relation to HF concentration.

The dependence of HF concentration on PL spectra has not been well studied. It is partly because the change does not cause formidable results as described above. Zhang et al. formed porous silicon with two kinds of HF concentration of 24 and 35%. But the anodization time is also varied in the literature. Further, there was no discussion on PL spectra [10].

The PL intensity shows interesting tendency as shown in Fig. 2. The figure shows PL area intensity dependence on HF acid concentration. PL area intensity is noticeably strong when HF acid concentration is 35 or 40%. It should be noted that the area intensity does not depend monotonically on HF acid concentration. This feature cannot be explained only by the electrochemical reaction expressed by [11]

$$\text{Si} + 2\text{HF} + (2 - n)\text{H}^+ \rightarrow \text{SiF}_2 + 2\text{H}^+ + ne^-$$

where $n < 2$, and $h^+$ and $e^-$ represent a hole and an electron, respectively. The PL intensity becomes low when the concentration of HF acid or ethanol is too small. Ethanol molecules contribute not only to the removal of hydrogen molecules from porous silicon during the reaction, but also to another chemical reaction. In other words, the feature implies that there exist the electrochemical reaction and another chemical reaction involved by ethanol at a time.

Actually, a post-anodization chemical treatment is critical to PL emission from porous silicon [12]. Therefore, we believe that ethanol plays an important role in the formation of light emitting porous silicon.

Zhang et al. reported an interesting fact of step-like behavior of photoluminescence peak energy dependent on HF concentrations [13]. They showed the PL results at HF concentrations under 30% in the case of p-type porous silicon, while our data were obtained between 30 and 50%. It is not rigorous to compare the results directly.

They did not take the ethanol into consideration, but they varied only the ratios of HF and water. Their PL spectra showed no variation in PL intensity through the experiment. It is consistent with their results that the intensity variation obtained in this article is related to ethanol concentration.

The ethanol is often used in the anodization to remove hydrogen gas from the porous silicon surface, but no evidence has reported so far that ethanol did not participate in the chemical reaction during the anodization. Our results suggest the reaction with ethanol as was also suggested in the chemical treatment in Ref. [12].

4. Conclusion

The HF acid concentration during anodization affects the PL intensity of porous silicon. When the concentration is 35 or 40%, the PL intensity is noticeably strong. This feature implies the existence of chemical reaction with ethanol together with the electrochemical reaction to form a porous structure.

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