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Photoluminescence of a silicon oxide film formed by anodization in the electropolishing region in HF solution

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Abstract. This paper reports the photoluminescence (PL) of a silicon oxide film formed by anodization in the electropolishing region in HF solution. The PL is preliminarily believed to be due to certain light-emitting centres in the silicon oxide film. In addition, the paper suggests that not all the PL of anodized silicon formed in HF solution can be solely ascribed to the porous silicon.

1. Introduction

The photoluminescence (PL) of porous silicon has been an attractive subject since Canham's [1] first report in 1990. Before this, the anodization of silicon in HF solution was investigated in detail by Zhang *et al* [2], who were convinced that the porous silicon is formed at current densities below a critical value, and above this value electropolishing of silicon occurs. In the literature, the 'PL of porous silicon' usually refers to the PL obtained from a sample prepared by anodization of silicon in the porous silicon formation region in HF solution. It is known that the current density regime for porous silicon formation or electropolishing of silicon depends on the conditions for anodization. This paper first investigates the anodic current–potential characteristics when silicon is anodized in HF solution. Then the current density regimes for porous silicon formation and electropolishing of silicon are defined. It is observed that the silicon oxide film formed by anodization in the electropolishing region in HF solution is photoluminescent. To our knowledge, this phenomenon is reported here for the first time.

2. Experiments

2.1. *Investigation of anodic current–potential characteristics for silicon anodized in HF solution*

In order to define the critical current density for the electropolishing of silicon under our experimental conditions, we investigated the anodic current–potential characteristics when silicon is first anodized in HF solution. A (111)-oriented p-type CZ silicon wafer with a resistivity of 1 Ω cm was used; one side of the wafer was polished, and on the other a thin aluminium film was deposited and subsequently metallized to form a good ohmic contact. Except for the exposed surface, the specimen and a copper strip for electrical contact were sealed with HF acid-proof wax. The electrolyte used for all experiments in this paper was

a solution of 40 wt% HF and deionized water. The volume ratio is 1:1. The cathode was a platinum grid. The reference electrode was a saturated calomel electrode (SCE). A Luggin capillary was used, whose tip was positioned about 2 mm away from the anode (silicon wafer). Both electrodes were vertically held in the cell. The anode potential was controlled with a potentiostat. For a given anode potential, a current was measured. Figure 1 shows the plot of the current versus the potential. The curve from the present experiment is similar to that given by Zhang *et al* as figure 1 in [2]. Both figures indicate the presence of different anodization regions when silicon is anodized in HF solution. In our experiment, the current increases exponentially with increasing anode potential in the region AB, which can be expressed in the form of Tafel's law:

$$V = -3.42 + 7.58 \ln i$$

where V is the anode overpotential and i is the current density. On the other hand, in the region CD, the current density remains at a relatively constant value of 60 mA cm^{-2}. According to the result of Zhang *et al* [2], the region AB in figure 1 is related to porous silicon formation, and the region CD to the electropolishing of silicon. From the electrochemistry, it is known that porous silicon formation is controlled by interfacial electrochemical reactions, while the electropolishing of silicon is limited by the diffusion of ions relating to the anodization.

2.2. *Photoluminescent film formation in the electropolishing region*

As shown in figure 1, the critical current density for the electropolishing of silicon in our experiment is 60 mA cm^{-2}. It has been demonstrated that the electropolishing of the silicon is preceded by the formation of oxide film with a critical thickness [2]. In the following experiment, when the silicon wafer is anodized in HF solution at a current density of 60 mA cm^{-2}, it was taken out of the electrolyte before the oxide film grew to the critical thickness. However, the oxide film was easily detached from the silicon substrate after the specimen had been dried. Under a UV lamp, the detached oxide film was found to be photoluminescent. Figure 2 shows the PL spectrum for the detached oxide film measured with an Hitachi 850 fluorine spectrometer. The wavelength of the exciting light was 250 nm, and the peak emission wavelength of the PL spectrum is about 600 nm. From the above results, it is reasonable to conclude that the silicon oxide film formed by anodization in the electropolishing region in HF solution is also photoluminescent, which means that not all the PL of anodized silicon formed in HF solution can be solely ascribed to porous silicon.

2.3. *X-ray photoelectron spectroscopy of the photoluminescent film formed in the electropolishing region*

According to Zhang *et al* [2] and Smith and Collins [3], the photoluminescent film formed in the electropolishing region is supposed to be silicon oxide. In order to confirm this, we first analysed the photoluminescent film formed in the electropolishing region by means of x-ray photoelectron spectroscopy (XPS). Figure 3 shows the detailed scan of the Si 2p region. On the curve, the low-binding-energy peak corresponds to Si^0, which shifts about 2.5 eV owing to sample charging. The high-binding-energy peak shifts about 6.5 eV compared with the Si^0 peak, which shows that the surface of the film is indeed in an oxidation state. However, the Si 2p binding energy of SiO_2 is only about 4 eV higher than that of Si^0. In view of the above facts, we believe that the high-binding-energy peak in figure 3 is from silicon oxide incorporating fluorine atoms which were introduced during anodization. Because the

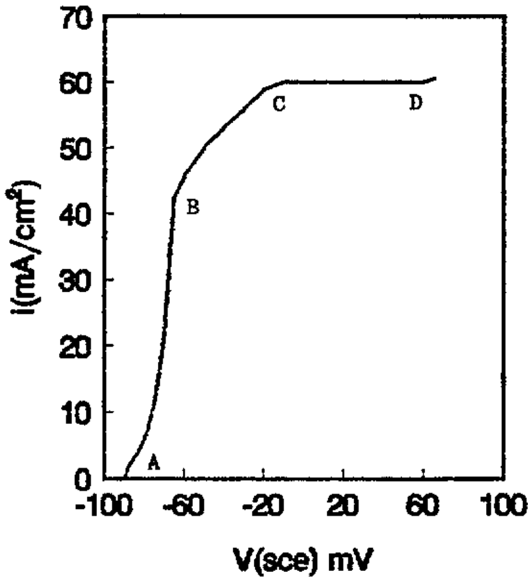


Figure 1. Anode current–potential characteristics of a p-type 1 Ω cm silicon wafer anodized in HF solution which consists of 40 wt% HF and deionized water (the volume ratio is 1:1).

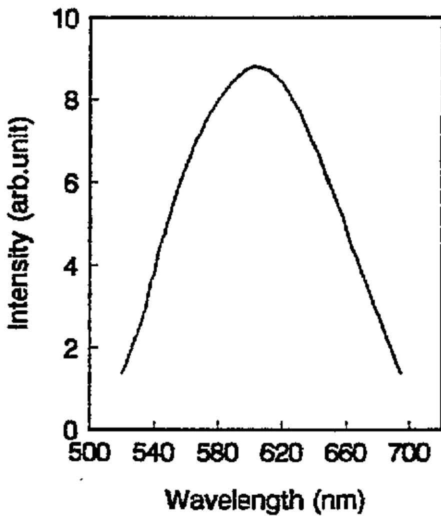


Figure 2. PL spectrum of the silicon oxide film formed by anodization in the electropolishing region in HF solution.

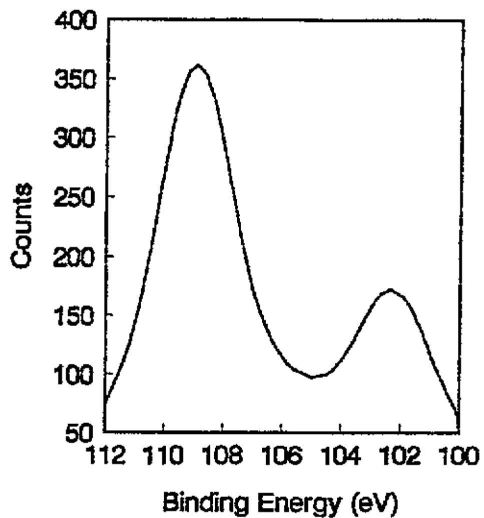


Figure 3. X-ray photoelectron spectrum of the Si 2p region from the photoluminescent film formed by anodization of silicon in the electropolishing region in HF solution. The spectrum is shifted approximately 2.5 eV to a high binding energy owing to sample charging.

electronegativity of fluorine is larger than that of oxygen, the introduction of fluorine into the silicon oxide further increases the binding energy of Si 2p electrons. However, other

factors probably contribute to the large shift in the high-binding-energy peak in figure 3, too.

2.4. Fourier transform infrared spectrum of the photoluminescent film formed in the electropolishing region

As mentioned above, XPS reveals that the surface of the photoluminescent film formed in the electropolishing region is oxidized. However, XPS can detect only the surface chemical composition of the photoluminescent film; so we further investigated its chemical composition by means of FTIR. The FTIR experiment was done with a Nicolet 170SX instrument. The photoluminescent film for the FTIR experiment was detached from the silicon substrate after the silicon had been anodized in the electropolishing region in HF solution. Figure 4 shows the FTIR spectrum of the detached photoluminescent film ranging from 400 to 1400 cm^{-1}. (It is in this region that Si–O bonds, if any, will be revealed). In figure 4, there are prominent absorption peaks at 1094, 904, 798, 662, 631 and 463 cm^{-1}. In order to obtain a convincing conclusion, we consulted [4] in which the FTIR spectra for opal (SiO_2nH_2O) and quartz (SiO_2) can be found. In the spectrum for opal, there are only three pronounced absorption peaks at about 1095, 785 and 472 cm^{-1} in the range 400–1400 cm^{-1} while, in the spectrum for quartz, there are pronounced absorption peaks at about 1085, 798, 788, 462 cm^{-1}, etc. Here we list only the absorption peaks concerned. In view of the above facts, the absorption peaks at 1094, 798 and 463 cm^{-1} in figure 4 could be assigned to silicon oxide. Considering the fact that the 1094 and 463 cm^{-1} peaks are the strongest in figure 4, we think that the matrix of the photoluminescent film formed in the electropolishing region is silicon oxide. In addition, figure 4 exhibits other absorption peaks such as Si–H_2 bonds at 904 cm^{-1} (scissor mode) and 631 cm^{-1} (wagging mode), Si–H bonds at 662 cm^{-1} (deformation mode), etc. As to the role that hydrogen plays in the PL of anodized silicon, this is a controversial topic [5–7]. In our experiment, we think it probable that the hydrogen atoms passivate the surface of oxide film, which reduces non-radiative centres such as dangling bonds. Figure 4 also shows a small shoulder near 610 cm^{-1} which is assigned to Si–Si bonds. This indicates that a few silicon atoms are embedded in the photoluminescent silicon oxide film. The above explanation of the FTIR spectrum is preliminary, and further study on the FTIR spectrum is required.

3. Discussion

As described above, the silicon oxide film formed in the electropolishing region is also photoluminescent. In the following, we shall discuss the formation of the silicon oxide film and its stoichiometry. From electrochemistry, it is known that oxide formation on a metal or semiconductor occurs only at a sufficiently high anode potential. After nucleation which is inhomogeneous, the oxide film expands on the surface and the thickness increases. If the oxide film is not condensable, it will crack while growing, and the anode potential for the oxide growth is equal to the initial value; on the other hand, if the oxide film is condensable, it will cover the whole surface continuously, and the anode potential for the oxide formation should be increased. From this theory and figure 1, it is deduced that the anodization of silicon in the electropolishing region in HF solution is the latter case as described above. Hence we believe that the silicon oxide film formed in the electropolishing region is condensable and continuous. Generally, the following reactions are considered as

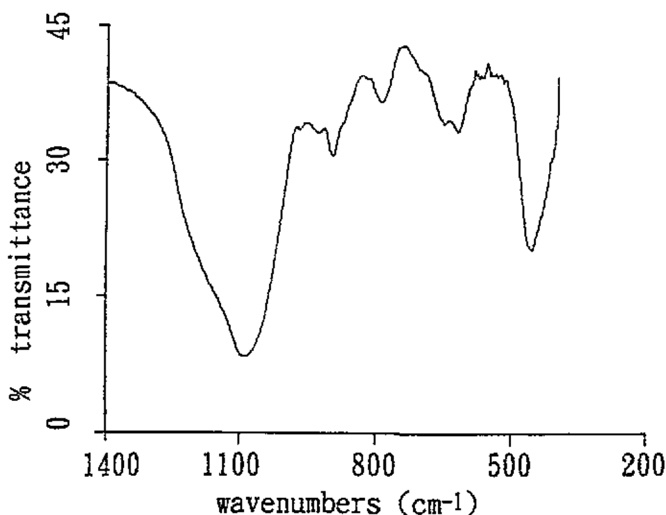
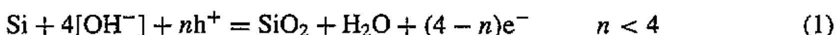


Figure 4. FTIR spectrum in the 400–1400 cm^{-1} region of the detached photoluminescent film formed by anodization of silicon in the electropolishing region in HF solution.

possible when silicon is anodized in HF aqueous solution [2, 8, 9]:



$$Si + 4[OH^-] + nh^+ = SiO_2 + H_2O + (4 - n)e^- \qquad n < 4 \tag{1}$$

$$SiO_2 + 6HF + H_2O = H_2SiF_6 + 2H_2O \tag{2}$$

$$Si + 2[F^-] + nh^- = SiF_2 + (2 - n)e^- \qquad n < 2 \tag{3}$$

$$SiF_2 + 4HF = H_2SiF_6 \tag{4}$$

where $[OH^-]$ is generated by electrolysis of H_2O, and h^+ and e^- represent a hole and an electron, respectively. The above reactions are thought to proceed simulataneously on the silicon surface and to compete with each other. In the electropolishing region, the current density is very large; so $[OH^-]$ ions increase strikingly owing to the electrolysis of H_2O; hence, the rate of reaction (1) increases, i.e. the formation of the silicon oxide is reinforced. In the meantime, the silicon oxide will be dissolved by HF acid. However, the oxide dissolution rate is lower than that of oxide formation; therefore, the whole surface of silicon wafer is completely covered by the oxide film, which will suppress reaction (3) and reaction (4). Further, we know that oxide formation occurs only at the silicon–oxide interface, and oxide dissolution occurs only at the oxide–solution interface. The $[OH^-]$ ions contributing to the anodization should diffuse through the oxide film and then participate in the oxide formation. In other words, the diffusion of $[OH^-]$ ions limits oxide formation; so the silicon is incompletely oxidized. In view of this, the stoichiometry of the silicon oxide formed in the electropolishing region could be expressed in terms of $SiO_x (x < 2)$, and x gradually decreases when the oxide film approaches the silicon–oxide interface. In fact, even the silicon oxide film formed by thermal oxidation is stoichiometrically deficient, too.

From the above analysis, it is known that the silicon oxide film is oxygen deficient, i.e. there are a number of oxygen vacancies in the film. In addition, the XPS experiment described above indicated that the oxide film incorporates fluorine atoms which probably

substitute for some oxygen sites. We preliminarily believed that certain defects such as oxygen vacancies or impurities such as fluorine atoms play roles in the PL of the silicon oxide film formed in the electropolishing region. Those defects or impurities possibly act as light-emitting centres. In addition, FTIR shows a few residual silicon atoms embedded in the oxide film; although the microstructure of the film has not yet been investigated, it does not rule out the possibility of nanometre-sized silicon clusters embedded in the oxide film. The PL of the silicon oxide film is also probably due to the quantum confinement in the silicon clusters which can also be considered as light-emitting centres. Recently, strong room-temperature PL of hydrogenated amorphous silicon oxide has been reported, which was ascribed to small amorphous silicon or single-crystal silicon clusters embedded in the matrix [10]. All our above views need further verification, which is in progress now. Here, it is worthwhile mentioning two other experimental results that have been reported in the literature. One is that a-SiO_2 irradiated with high-energy electrons can be photoluminescent; this is believed to be due to self-trapped exciton consisting of an oxygen interstitial and an oxygen vacancy [11]. The other is the light emission phenomenon during anodic oxidation of silicon in KNO_3 solution, which is believed to be due to the inelastic scattering of hot electrons within the light-emitting centre in the SiO_2 layer [12]. Both results suggest that the PL of silicon oxide from a light-emitting centre is believable.

4. Conclusions

The anodic potential characteristics when silicon is anodized in HF solution under specific conditions have been investigated, and the critical current density for electropolishing of silicon has been defined. It is shown that the silicon oxide film formed by anodization in the electropolishing region is photoluminescent. From the analysis of the silicon–solution interfacial reactions and by means of XPS as well as FTIR, we think that the chemical composition of the oxide film is SiO_x ($x < 2$) incorporating fluorine and hydrogen atoms, and containing a few silicon atoms. It is preliminarily believed that certain light-emitting centres such as oxygen vacancies or fluorine atoms which substitute for the oxygen sites play important roles in the PL of the silicon oxide film formed in the electropolishing region. However, it does not rule out the possibility of quantum-sized silicon clusters responsible for PL of the silicon oxide film. As to the hydrogen, it is believed to be a surface-passivating agent which reduces non-radiative centres, thus benefitting the PL of silicon oxide. Further studies are in progress now to verify the above views. In addition, it seems that not all the PL of anodized silicon formed in HF solution can be ascribed to porous silicon.

Acknowledgments

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