Formation of luminescent \((\text{NH}_4)_2\text{SiF}_6\) phase from vapour etching-based porous silicon

M. Saadoun\textsuperscript{a}, B. Bessaïs\textsuperscript{a,*}, N. Mliki\textsuperscript{b}, M. Ferid\textsuperscript{c}, H. Ezzaouia\textsuperscript{a}, R. Bennaceur\textsuperscript{a}

\textsuperscript{a}Groupe de Photovoltaïque et des Matériaux Semi-conducteurs, Laboratoire des Applications Solaïres, Institut National de Recherche Scientifique et Technique, BP 95, 2050 Hammam-Lif, Tunisia

\textsuperscript{b}Laboratoire “Matériaux: Organisation et Propriétés”, Département de Physique, Faculté des Sciences de Tunis, 1060 Le Belvédère, Tunis, Tunisia

\textsuperscript{c}Laboratoire des Procédés Chimiques, Institut National de Recherche Scientifique et Technique, BP 95, 2050 Hammam-Lif, Tunisia

Received 23 June 2002; received in revised form 1 November 2002; accepted 22 January 2003

Abstract

In this paper we describe the formation of a luminescent \((\text{NH}_4)_2\text{SiF}_6\) via porous silicon (PS) obtained from HNO\textsubscript{3}/HF vapour etching (VE) silicon (Si) substrates. It was found that at specific conditions, PS transforms in a luminescent thick white powder (WP) layer. Scanning electron microscopy (SEM) revealed that the WP has a coral-like structure. It was also found that PS persists as an intermediate layer between the Si substrate and the WP, and seems to be the seed that transforms into the WP. SEM microanalysis show that the WP is essentially composed of silicon (Si), nitrogen (N) and fluorine (F). Fourier transform infrared (FTIR) spectroscopy investigations show that this WP contains SiF\textsubscript{6}\textsuperscript{2−} and NH\textsubscript{4}\textsuperscript{+} ions and N–H chemical bonds. X-ray diffraction (XRD) patterns of the WP confirm that a \((\text{NH}_4)_2\text{SiF}_6\) cubic phase is concerned. SEM microanalyses show an excess of Si in the WP matrix. FTIR spectroscopy and XRD analysis reveal the presence of crystalline Si particles and SiO\textsubscript{x}, both originating from the excess of Si. The \((\text{NH}_4)_2\text{SiF}_6\) WP phase emits an intense photoluminescence (PL) band, shifted towards higher energies as compared to the starting PS layer. The possible origin and mechanism of the luminescence emission was discussed taking into account the ability of small SiO\textsubscript{x}-surrounded Si particles to emit PL at rather high energy. The wide range variation of the thickness of the \((\text{NH}_4)_2\text{SiF}_6\) WP may be easily used for the grooving of Si wafers.

© 2003 Elsevier Science B.V. All rights reserved.

PACS: 68.55.Ac; 68.37.Hk; 61.43.Gt; 78.30.Ly; 78.55.Mb

Keywords: Silicon; Etching; Porous silicon; Ammonium silico-fluoride; Luminescence

1. Introduction

Chemical and electrochemical etching techniques based on HF solutions were widely used to produce a large variety of porous silicon (PS) structures [1,2] that can be applied in various silicon-based devices. However, the latter methods have some limits especially in large area applications. On this basis other simple etching methods alternatives to conventional techniques, suitable for their applications in some silicon devices, have been developed [3,4]. A simple and low cost vapour etching (VE) technique using a mixture
of HNO₃/HF acid solutions have been recently employed [4]. The VE technique enables to produce homogeneous and highly luminescent PS layers [4]. However, we noticed that at specific conditions, the VE method might transform the PS layer in a luminescent powder-like phase, identified as being the (NH₄)₂SiF₆ compound. This finding was inciting us to perform deeper investigations in order to understand how VE-based PS transforms in a luminescent powder. In this paper, we detail the formation of the (NH₄)₂SiF₆ powder-like phase, and point out some of its structural and luminescence properties. Finally, we present a technological potential use of this powder in silicon micro-machining.

2. Experimental procedure

The principle of the VE method consists of exposing crystalline Si substrates of various doping types to acid vapours issued from a mixture of HNO₃ (65%) and HF (40%) [4]. It was found that VE of silicon results in the formation of porous silicon (PS). Investigations on the VE-based PS morphology do not show significant differences between p- and p⁺-type PS structures [4]. Therefore, in this study we only use p-type (ρ = 2 Ω cm) oriented Si substrates having mirror-like surfaces. In order to obtain homogeneous luminescent PS layers, we need to control the etch kinetics, and hence all the determining experimental factors: the HNO₃/HF volume ratio, the temperature of the acid mixture and the exposure time of the Si substrate to the acid vapours. Surprisingly, we noticed that when silicon is vapour etched at HNO₃/HF volume ratio ranging between 1/6 and 1/2 (the total volume is about 2 l), a large part of PS transforms in a luminescent white powder (WP). Scanning electron microscopy (SEM) microanalysis, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and photoluminescence (PL) measurements were used to characterise the WP.

3. Results and discussion

Fig. 1 shows a PS layer obtained from the VE technique. In fact, in order to obtain such homogeneous PS layers, the preparation parameters should vary in a limited range of values [4]. Indeed, beyond a certain etching time (depending on the temperature of the acid solution), vapour condensation could occur leading to degradation or to partial destruction of the PS layer. In order to prevent undesirable acid vapour condensation [4] that may limit the etching progress and hence the formation of rather thick and controllable thickness, we estimated that we should slightly raise the temperature of the Si substrate. At these conditions, and for rather long etching periods, we noticed the formation of a white powder (WP), which was found to be highly luminescent. In fact, PS was found to be a major phase above a HNO₃/HF volume ratio of 1/9, while the WP phase becomes major at HNO₃/HF volume ratio ranging between 1/6 and 1/2. Obviously, one may deduce that the WP is preponderant for HNO₃/HF volume ratio in the range of 1/6–1/2.

Fig. 1. SEM cross-section view of a PS layer prepared by VE p-type (1 0 0) oriented Si wafer. The HNO₃/HF volume ratio is 1/8, the exposure time is 15 min and the temperature of the acid solution is 30 °C.

Scanning electron microscopy (SEM) plan view (Fig. 2a) shows that this WP has a coral-like structure (Fig. 2). From cross-section SEM view (Fig. 2b), it is worth noting that the PS layer persists as an intermediate layer between the Si substrate and the WP. From the SEM image of Fig. 2b, one may guess that PS (the minor phase) is the seed that transforms into the WP, since at short etching periods and without substrate heating, only the PS phase forms (Fig. 1).

First SEM microanalysis (Fig. 3) shows that this powder is essentially composed of silicon (Si), nitrogen (N) and fluorine (F). The latter elements
Fig. 2. (a) Surface SEM plan view of the white powder; (b) SEM cross-section view of the white powder. The HNO₃/HF volume ratio is 1/2, the exposure time is 60 min, the temperature of the acid solution is 40 °C, and the temperature of the substrate is 40 °C.
constitutes approximately 63 wt.% of the powder (Fig. 3). Hydrogen is abundant in the HF/HNO₃ etching mixture, hence it is reasonable to suspect its presence, but it cannot be probed by SEM microanalysis. Furthermore, one may notice an excess of Si corresponding approximately to 3 wt.% of the WP. On the other hand, no oxygen was clearly evidenced by SEM microanalysis, except whether it exists in form of traces. The Si excess could be in form of free particles, or forming other minor phases like SiOₓ (x ≤ 2). Thus, in order to get more information on the other elements that the WP could contain, the latter complex structure was investigated by FTIR spectroscopy and XRD. The FTIR spectrum (Fig. 4) of the WP shows that major absorption peaks correspond to SiF₆²⁻ and NH₄⁺ ions together with N–H chemical

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>18.66</td>
<td>25.11</td>
</tr>
<tr>
<td>F</td>
<td>63.29</td>
<td>62.78</td>
</tr>
<tr>
<td>SiK</td>
<td>18.05</td>
<td>12.11</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 3. SEM microanalyses spectrum of the white powder.

Fig. 4. FTIR spectrum of the white powder in the 400–4000 cm⁻¹ spectral range.
bonds, species not observed in VE-based PS layers. These first analysis enable us to predict the chemical formula of the WP as being the \((\text{NH}_4)_2\text{SiF}_6\) compound (ammonium silico-fluoride). Nevertheless, one can notice small absorption peaks (Fig. 4) inside both A and B spectral zones. Let us now analyse these two zones. Fig. 5a and b depict FTIR spectra corresponding to A and B spectral zones. The A zone (Fig. 5a) shows resolved structures corresponding to Si–Si stretching modes (610–620 cm\(^{-1}\)). The B zone (Fig. 5b) lies in the 970–1300 cm\(^{-1}\) spectral range; it shows other resolved structures attributable to CH\(_2\) stretching modes (1288–1301 cm\(^{-1}\)) in SiCH\(_2\), to the LO phonon line in thin SiO\(_x\) layer (1217 cm\(^{-1}\)), to the Si–O–Si stretching mode (1106 cm\(^{-1}\)), and to the Si–O stretching mode (1150 cm\(^{-1}\)) (essentially encountered in deeply oxidised PS layers [5]). One may also guess (Fig. 5b) the existence of the TO phonon line in thin SiO\(_x\) layer (1067 cm\(^{-1}\)) and the Si–O bending mode (978 cm\(^{-1}\)), which overlap with the Si–O–Si stretching mode and the large SiF\(_6^{2-}\) mode, respectively. From these first FTIR analyses one may presume that the WP
phase contains other minor phases and species particularly SiO$_x$ and Si. At this stage, we cannot say whether Si is in form of free particles or embedded in a SiO$_x$ matrix.

X-ray diffraction (XRD) patterns of the WP (Fig. 6) confirm that a (NH$_4$)$_2$SiF$_6$ cubic phase is concerned. Now, it will be interesting to deeply examine the XRD patterns and to confirm whether free Si particles exist inside the (NH$_4$)$_2$SiF$_6$ phase. By zooming the XRD spectrum (Fig. 7a–c), one may notice small peaks, not belonging the (NH$_4$)$_2$SiF$_6$ phase. XRD spectra of Fig. 7a–c demonstrate the existence of (1 0 0), (1 1 1) and (2 2 0) oriented Si particles. The (1 1 1) XRD line is more intense than the other two lines, since it likely corresponds to the denser plane in Si, while the (2 2 0) line is overlapped by the (3 1 1) line of the (NH$_4$)$_2$SiF$_6$ phase. These XRD analysis (Figs 7a–c) clearly demonstrate that Si particles exist in the (NH$_4$)$_2$SiF$_6$ WP phase. However, we still cannot say whether the Si particles are free or embedded in a SiO$_x$ matrix. Nevertheless, one may guess that pure free Si particles do not exist in such (NH$_4$)$_2$SiF$_6$ complex matrix, so we believe that small Si particles are more or less surrounded by thin SiO$_x$ layer or Si–O bonds.

In the past, low temperature vapour (LTV) deposition has been used by Heimann et al. [6] to form films on Si wafers from NO$_2$–HF–H$_2$O gas mixtures. They did not mention any porous layer formation. However, they reported the formation of films composed of a cubic (NH$_4$)$_2$SiF$_6$ phase and SiO$_x$, with small amounts of the trigonal β-(NH$_4$)$_2$SiF$_6$ phase. We believe that the formation mechanisms leading to the formation of the (NH$_4$)$_2$SiF$_6$ from the VE-based PS do not present great differences from what has been reported by Heimann et al. [6]. As has been shown by FTIR spectroscopy (Fig. 5b) a small amount of SiO$_x$ exists in the (NH$_4$)$_2$SiF$_6$ WP matrix. Depending on the HNO$_3$/HF volume ratio and the etching time, one may obtain thin or thick WP layers. The amount of the SiO$_x$ could depend on the depth of the WP phase. Indeed, thin WP layers enable acid vapours to easily diffuse inside the porous medium and then favour more or less the reaction leading to the formation of Si–O$_x$ and Si–O bonds. It becomes clear that deeper investigations are needed to understand the competitor actions of HF and HNO$_3$ particularly regarding the formation of Si–O$_x$ and Si–O bonds.

The (NH$_4$)$_2$SiF$_6$ WP phase emits an intense PL band (Fig. 8), shifted toward higher energies as compared with that of a VE-based PS layer. FTIR and XRD analyses of the (NH$_4$)$_2$SiF$_6$ clearly show that the Si excess, detected (in a first step) by SEM microanalyses,
Fig. 7. Detailed XRD patterns showing the existence of different Si orientations: (a) (100), (b) (111) and (c) (220).
exits in forms of SiO\(_x\) and Si particles. The \(\text{(NH}_4\text{)}_2\text{SiF}_6\) WP exhibits a broad PL band having an energy peak position close to 2.1 eV. The WP continues to be luminescent after having been dissolved in water. However, the PL emission completely disappears by adding to the ionic solution some drops of HF or NaOH (1N). Thus, one may guess that the PL band emission originates from Si particles surrounded by SiO\(_x\) and obviously not from the ionic species of the \(\text{(NH}_4\text{)}_2\text{SiF}_6\) phase. In a previous work [4], transmission electron microscopy (TEM) observations revealed that VE-based PS is essentially composed of dots-like crystalline Si particles embedded in an amorphous phase, with sizes not exceeding 5 nm. They emit a PL band with peak energy close to 1.9 eV. The formation conditions of the \(\text{(NH}_4\text{)}_2\text{SiF}_6\) WP let us presume that the size of the Si particles belonging the WP are smaller than that of the VE-based PS [4]. At a first sight, one may assume that the PL band blue-shift related to the \(\text{(NH}_4\text{)}_2\text{SiF}_6\) is due to radiative recombination in small Si–O passivated Si particles, whose band gap opens by quantum confinement. However, it has been demonstrated [7] that when the Si particle sizes are larger than 3 nm quantum confinement alone can explain the PL blue-shift even whether Si–O bonds surround them. However, the recombination mechanisms become different when the Si–O passivated Si particle sizes are less than 3 nm. In this latter case, depending on the size of the particles, trapped electrons or excitons on Si–O bonds are involved [7]. When excitons are concerned, the peak of the emission energy reaches an upper limit around 2.1 eV, which is independent of size. Consequently, one may attribute the 2.1 eV peak energy of the WP to trapped excitons in Si–O bonds. Oxygen vacancies at the Si/SiO\(_x\) interface gives luminescence in the 2–2.2 eV range [8], and could contribute to the observed PL emission, particularly in this range of energy. However, by changing the formation conditions of the \(\text{(NH}_4\text{)}_2\text{SiF}_6\) WP (i.e. HNO\(_3\)/HF volume ratio and etching time), we noticed PL peak energy below 2 eV. Hence, we can apparently change the size of the Si particles and limit the action of the SiO\(_x\) minor phase, so that we can more or less tune the PL of the WP. Clearly, various WP preparation conditions should be investigated by correlating FTIR and PL results to resolve explicitly the PL mechanism.

The \(\text{(NH}_4\text{)}_2\text{SiF}_6\) white powder may be easily removed from the silicon substrate simply by deeply blowing air on the Si substrate or by dipping it in water. This enables us to form hemispherical grooves on silicon (Fig. 9) with different depths, with an accuracy of 0.2 \(\mu\)m. After removing the WP, a thin porous layer remains on the grooved zone (Fig. 7). The hemispherical grooves could be interesting to be
introduced in microelectronic engineering, micro-machining as well as for buried metal contact in solar cells processing.

4. Conclusions

We have shown, for the first time, that a luminescent (NH$_4$)$_2$SiF$_6$ white powder (WP) phase may be produced by vapour etching silicon. A growing PS layer was found to be the first seed that enables to start the formation of this powder. The formation kinetics of the (NH$_4$)$_2$SiF$_6$ white powder was found to depend on both acid mixture and silicon substrate temperatures. SEM, FTIR and XRD investigations of the WP show the existence of an excess of Si probably forming SiO$_x$-surrounded crystalline Si particles from which visible PL emission originates. The simple removal of the (NH$_4$)$_2$SiF$_6$ white powder enables us to selectively groove silicon. The VE method could introduce new applications for both VE-based PS and the (NH$_4$)$_2$SiF$_6$ related material. The (NH$_4$)$_2$SiF$_6$-associated grooving technique could open new horizons and perspectives in silicon micro-machining as well as for efficient silicon solar cells.

Acknowledgements

This work was supported by the Secretary of State of Scientific Research and Technology (PRC 98).

References