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Simultaneous platinum deposition and formation of a photoluminescent porous silicon layer

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Abstract

A method is presented for simultaneously producing porous silicon and depositing platinum on silicon from a platinum and fluoride solution operating at the rest potential. The resulting layers display visible photoluminescence. Quantitative electrochemical measurements demonstrate that the platinum ions act as an oxidizing agent for silicon, and that the silicon oxidation reaction proceeds in the porous silicon regime when the solution parameters are properly chosen. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electroless metal deposition; Fluoride solutions; Stain etch; Porous silicon; Electric contacts

1. Introduction

The discovery of the photoluminescent properties of porous silicon (PS) [1] has made it possible to employ silicon in optoelectronic devices. The formation of PS displaying intense photoluminescence in the visible range has been widely studied ever since, and extensively reviewed very recently [2]. However, due to its porous nature, the material is considerably fragile and the pore surface is difficult to access, which complicates the preparation of high-quality solid electric contacts necessary to produce electroluminescence in a practical device. Physical vapor deposition of gold, aluminum and ITO glass is usually employed to fabricate electric contacts on PS, although this technique provides little penetration of the conducting material into the pores. Several attempts have also been made to deposit metals by electroless or electrochemical means on PS layers grown previously using a different process [3–5]. We present here a novel method for simultaneously producing photoluminescent layers and depositing metal on a p-type silicon surface from solutions containing metal and fluoride ions.

PS formation is based on silicon oxidation and dissolution of the oxidation products. These processes result in the formation of corrosion structures (pores) that create sponge-like crystalline layers several microns deep [6] or in thin layers of porous amorphous material [7]. In order to produce these porous layers, the holes necessary for silicon oxidation [8] must be supplied to the surface in the presence of species that can dissolve the oxidation products (fluoride solutions are usually employed). Typically, two methods of fabricating PS exist (see Fig. 1, left):

1. Anodization: a controlled positive bias (and illumination in the case of low doped n-type samples) is applied to the silicon samples with respect to a reference in solution [4]. This results in the accumulation of holes at the semiconductor surface and their continuous supply through the circuit as the silicon is oxidized [8].

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2. Stain etch: a chemical species that oxidizes silicon directly (an oxidizing agent, usually HNO_3 [7] although others can be employed [9]) is added to the fluoride solution. NO_2, a derivative of HNO_3, has a strong tendency to reduce to the (soluble species) NO_2^- by gaining electrons from the bonding levels of the silicon [10]. This is regarded as the injection of a hole [8] into the silicon valence band, and thus the hole concentration in the silicon surface is controlled by the supply of the oxidizing agent to the interface with the solution [10]. Neither an external bias nor illumination for the n-type samples are required in this case, and the reaction proceeds at the rest potential.

Our method employs an oxidizing agent in the fluoride solution as in the stain etch. It is based on (a) the choice of an oxidizing agent whose reduced form is a metallic deposition on the surface, and (b) the control of the hole injection current from the oxidizing agent into the silicon so that it results in the formation of PS.

2. Experimental

In order to tune the process, the energy diagram of the system must be determined and the currents crossing the silicon | solution interface have to be accurately measured. For that purpose, the measurements were

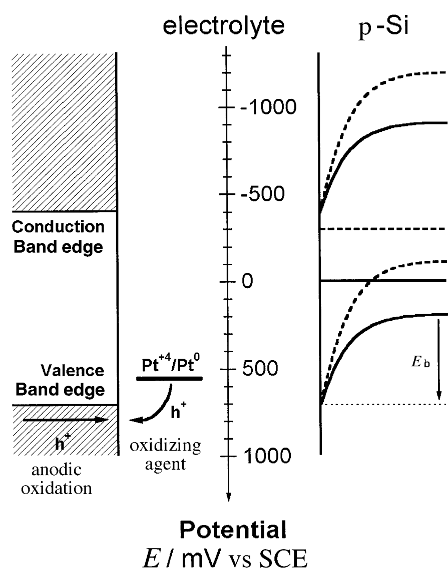

Fig. 1. Left: diagram of a semiconductor (electrolyte interface showing the hole (oxidation) currents under positive bias and in the presence of an oxidizing agent. The conduction and valence band edges correspond to silicon in the deposition solution, and the Pt^{4+}/Pt redox couple (having a reduction potential E_{Pt}) acts as the oxidizing agent. Right: complete band diagrams for a p-type silicon sample immersed in the fluoride solution (blank, dashed line) and after addition of the platinum ions (deposition, solid line). The determination of the band edges and the band bending E_b is explained in the text.

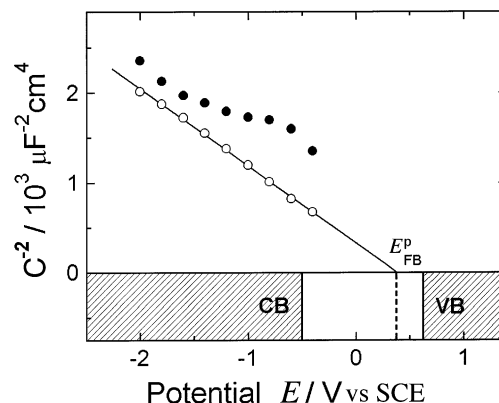

Fig. 2. Mott–Schottky plots of p-Si in a 2 M fluoride solution, before (●) and after (○) the electropolishing procedure described in the text. The plot becomes perfectly linear and the extrapolated flatband potential E_{FB} is very reproducible. The conduction and valence bands (CB and VB, respectively) have also been indicated.

carried out under potentiostatic control and in the dark in a three-electrode electrochemical cell using a Solartron 1287 electrochemical interface and a 1255 frequency response analyser. The reference electrode in solution was a saturated calomel electrode (SCE) and a platinum grid was used as a counter electrode. Samples were p-type silicon (100) having a resistivity of 1 Ω cm (Siltronix). A platinum wire of purity 99.99% (Goodfellow) was also used as a sample for some measurements. The deposition solution was prepared by adding 1 mM K_2PtCl_6 (Johnson–Matthey) to a 2 M fluoride solution (pH 1) prepared from 40% HF (Merck) and ultrapure water (Milli-Q, Millipore). The band diagram of the silicon | electrolyte interface and the hole injection currents were determined in the deposition solution. The silicon oxidation currents were measured both in the deposition solution and in a 2 M fluoride solution without the addition of platinum ions ('blank' solution). The rest potential E_{Pt} of a platinum wire immersed in the deposition solution was estimated as the potential drop between the reference electrode and a platinum wire in equilibrium with the solution containing platinum ions. Silicon flatband (FB) potentials E_{FB} were determined by measuring the silicon | electrolyte junction capacitance at 25 kHz and using the Mott–Schottky relationship [11]. In order to obtain reproducible FB measurements, the samples were previously electropolished as described in [12]. The electropolishing conditions were +4.0 V (SCE) in a 0.6 M NH_4F solution at pH 4.5 for 15 min, yielding a current of about 1 mA. The samples were subsequently dipped in concentrated HF to remove the remaining oxide. Mott–Schottky plots in the blank solution, before (●) and after (○) this procedure are shown in Fig. 2, together with the extrapolated value of E_{FB} and the position of the silicon bandgap in the potential scale. Once the conditions for PS formation had been deter-

mined, the Pt-coated photoluminescent silicon samples were prepared at the rest potential, i.e. by simply immersing the substrates without the application of an external bias ('electroless' deposition). Previous morphological and elemental characterization of similar platinum deposits has been presented elsewhere [13].

3. Results and discussion

The choice of platinum ions as the oxidizing agent for silicon was supported by the following measurements. In order to determine the relative energetic position between the silicon band edges and the platinum redox level in the electrolyte (i.e. the energy of the electrons involved in the platinum reduction and oxidation reactions), we measured the rest potential E_{Pt} of a platinum wire immersed in the deposition solution, and the flatband potential E_{FB} of a silicon sample immersed in the same solution. Very reproducible values of $E_{Pt} = +0.55$ V versus SCE and $E_{FB} = +0.50$ V versus SCE were obtained. The extrapolation of the Mott–Schottky plot is shown in Fig. 2 and is in good agreement with previously reported results [12], taking into account that the solution pH produces a shift in the FB potential of -60 mV (SCE) [14]. The position of the valence band edge (E_V) with respect to the reference in solution can be calculated by assuming that the valence band is located at about 0.20 V below the Fermi level for p-Si 1 Ω cm (doping level 10^{16} cm^{-3}) at 300 K [15]. Thus $E_V = E_{FB} + 0.20 = +0.70$ V versus SCE, and the platinum redox level is directly given by $E_{Pt} = +0.55$ V versus SCE. In addition, the rest potentials E_{Si} of the silicon electrode in the blank solution (-0.3 V (SCE)) and after adding the platinum ions (0 V (SCE)) allow us to sketch the band bending E_b for each case, since $E_b = E_{FB} - E_{Si}$. These have been depicted in Fig. 1 (right). As can be seen, the platinum redox level lies very close to the silicon valence band edge and, therefore, they can efficiently exchange charge. In our case, platinum ions reducing (i.e. depositing) at the silicon surface produce a hole injection current into the semiconductor, as we will immediately see.

The hole injection current due to the platinum ions can be measured by collecting the holes under negative bias [16]. Note that the negative bias prevents holes from being captured at the surface and, therefore, the semiconductor cannot be oxidized (this is in contrast with the situation at the rest potential or at more positive potentials). Fig. 3 shows the current–potential plot of the p-Si electrode in the blank solution (A) and in the deposition solution under increasing stirring conditions (B, C, D). These curves were obtained at a scan rate of 50 mV s^{-1} towards negative potentials, immediately after immersion of the electropolished and oxide-free samples in the corresponding solution. In the absence of oxidizing agents, the semiconductor | electrolyte interface behaves like a diode and curve A corresponds to the leakage (reverse) current. The current plateaus in curves B, C, D demonstrate that hole injection from the platinum ions in the deposition solution is a process limited by the diffusion of platinum ions to the silicon surface. This is confirmed by the equivalent current plateau that is obtained at a platinum wire electrode (curve E) in the same solution and stirring conditions as curve D. Therefore, hole injection from the platinum ions into the silicon valence band is limited by mass transport to the interface and the injection current can be augmented by increasing either the stirring of the solution or the platinum concentration in solution. The hole injection current produces a downwards shift on the entire current–potential curve (see also the inset in Fig. 4), and correspondingly shifts the silicon rest potential to more positive values. This behavior of the silicon | electrolyte interface under hole injection is similar to that of a semiconductor | metal junction under illumination (solar cell).

The effect of the injection current on the silicon can be outlined qualitatively as follows: in the conditions employed for the preparation of the platinum-deposited samples (rest potential, i.e. net current zero) the injection current must balance the silicon oxidation current (of the same amount and opposite sign). To provide such a current, the bending of the bands at the silicon surface is lowered to favor the anodic process, and in the presence of fluoride ions in the solution this results in the simultaneous oxidation of silicon. In other words, the holes injected from the platinum ions in solution are captured at the silicon surface, thus allowing the oxidation of silicon. Note that although the Fermi level of silicon approaches E_{Pt} after immersion in the deposition solution, these levels are not equalled, as

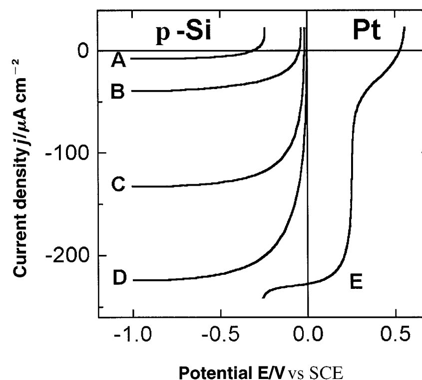

Fig. 3. Leakage current (A) of a p-type silicon sample in the blank solution (2 M fluoride) and diffusion-limited hole injection currents (B, C, D) for increasing stirring in the deposition solution (2 M fluoride, 1 mM K_2PtCl_6). For the same conditions as D, a similar plateau is found in a platinum sample (E).

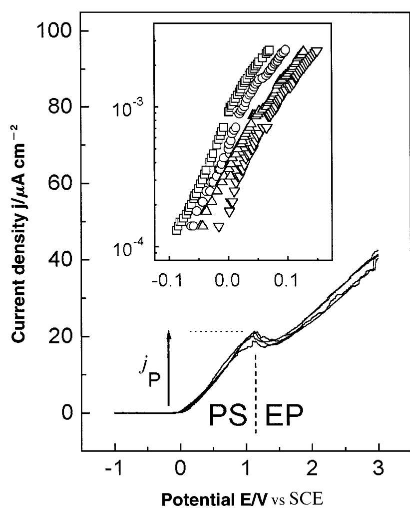

Fig. 4. Oxidation current in a p-type silicon sample immersed in the blank and platinum deposition solutions. The peak current density j_P sets the border between the porous silicon and electropolishing regimes (labeled PS and EP, respectively). Inset (units as outer frame): Tafel plots in the porous silicon region for the blank solution (□) and in the platinum deposition solution without stirring (○) and under increasing stirring (△,▽).

this would correspond to thermodynamic equilibrium. Instead, the system reaches steady-state when the currents in both directions balance and yield net zero current.

To study in detail the effect of a given injection current on the silicon immersed in the blank and deposition solutions, we applied positive potentials to the silicon samples and measured the current flowing through the surface. The resulting current–potential plots (Fig. 4) display a current peak and an exponential dependence in the region to the left of the peak (see figure inset), which are characteristic of the anodic oxidation of silicon in aqueous fluoride solutions. They are interpreted in this way: positive potentials bend the semiconductor bands upwards, thereby increasing the hole concentration at the silicon surface. The anodic current that is measured corresponds to holes flowing from the silicon bulk towards the interface and is associated with silicon oxidation. The value of this oxidation current density is given by the Tafel equation [8]:

$$j_{ox}(E) = j_S \exp(\alpha_a ze(E - E_{Si})/kT) \quad (1)$$

where α_a is the anodic transfer coefficient and E_{Si} the rest potential of the silicon electrode. The inset of Fig. 4 shows that in the region to the left of the current peak, the supply of holes to the interface is rate limiting [17] regardless of the presence of platinum and the stirring conditions. The slope of the Tafel plot (inset) is 112 mV decade^{-1}, which yields $\alpha_a z = 0.53$, in good agreement with [17]. As mentioned above, the current–potential curve in the blank solution (□) is shifted downwards by the presence of platinum ions in the non-stirred solution (○) and under increasing stirring (△,▽). The region to the left of the peak actually corresponds to the PS formation regime and it is characterized by an excess fluoride concentration that readily dissolves the oxide that is formed, keeping the silicon surface H-terminated [17]. Beyond the current peak, the silicon band bending and thus the hole concentration and the oxidation rate are too high, so that the chemical dissolution of the oxide becomes rate limiting: the fluoride solution can no longer dissolve the oxidation products and an oxide layer is condensed at the surface. This is the onset of the electropolishing regime [18].

The peak current density value, j_P, sets the border between the PS and electropolishing regimes in a solution of given fluoride concentration and pH. If the hole current (either due to an external bias or to compensation of the injection from an oxidizing agent) is lower than j_P, the corresponding band bending in the silicon will be below the transition between the PS and the electropolishing regimes (Fig. 4). In that case, the silicon oxidation reaction will proceed in the PS regime and the resulting material can in principle be photoluminescent. On the other hand, if the hole current exceeded j_P the system would drop in the electropolishing regime, thereby forming an oxide layer at the silicon surface. An extensive study of j_P and other characteristic currents of the silicon | fluoride interface can be found in Chazalviel et al. [19].

As can be seen in Fig. 4, $j_P \cong 20$ mA cm^{-2} for both the blank and the deposition solution and regardless of the stirring conditions. Setting the stirring of the deposition solution so that the injection current was always below 20 mA cm^{-2}, and withdrawing the silicon samples well before coalescence of the platinum deposit to avoid complete metal coverage, we obtained samples that are photoluminescent in the visible range as is shown in the spectrum of Fig. 5. Whatever is the

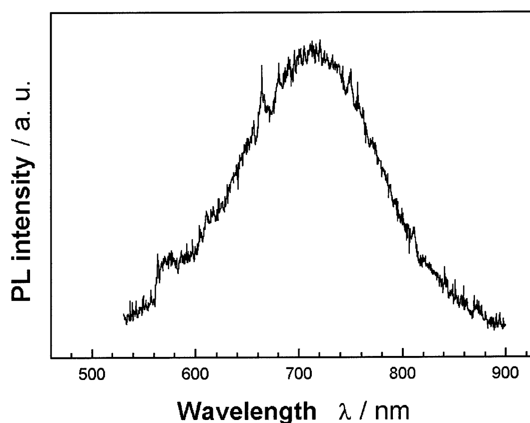

Fig. 5. Photoluminescence spectrum of a p-type silicon sample after platinum deposition at 50 μA cm^{-2} for 60 min.

mechanism for photoluminescence emission in PS, we believe that there is enough evidence to attribute the photoluminescent properties of these samples to the formation of PS simultaneous to (and as a result of) the platinum deposition in fluoride media. Provided that the silicon oxidation reaction is kept in the PS regime by using the method described here, stronger corrosion currents and hence thicker PS layers should be obtained for deposition solutions having higher fluoride and platinum concentrations. Of course, the platinum deposition rate will also be higher in those solutions and this can happen to be a disadvantage, because photoluminescence emission can be physically blocked if coalescence of the metal deposit is achieved. A careful tune-up of the method is still necessary in order to obtain efficient photoluminescence, and further work is in progress in order to characterize the porous material and other aspects of the process. This study has been carried out on p-type silicon although similar results can be obtained on low-doped n-type samples. Of course, no illumination is necessary to produce PS on n-Si with the method described here, because the holes are injected from platinum ions in the solution.

4. Conclusions

In summary, a method is presented for simultaneously depositing platinum and producing porous silicon from a platinum and fluoride solution operating at the rest potential. When immersed in such solutions, silicon undergoes a spontaneous anodization process as a result of the metal deposition in fluoride media. The method thus consists in the choice of the platinum ion mass transport conditions that result in an injection current below ∪5the maximum current for PS formation. Samples prepared in this way display visible photoluminescence.

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