Correlation Between Surface Non-Radiative Recombination and Current Oscillation at p-Si(100) During Electropolishing in Fluoride Solution

J. Rappich[1], V. Yu. Timoshenko[2], and Th. Dittrich[3]

[1]) Hahn-Meitner-Institut, Abt. AP, Rudower Chaussee 5, D-12489 Berlin, Germany

[2]) Moscow State University, Physics Department, 119899 Moscow, Russia

[3]) Technische Universität München, Physik-Department E16, D-85747 Garching, Germany

The electropolishing of p-Si(100) in aqueous NH₄F solution is investigated in-situ by photoluminescence (PL) with short N₂-laser pulses. The PL signal increases with potential and reaches a maximum when current oscillations occur. The PL signal oscillates with the same period but anticorrelated to the current. The thin anodic oxides are removed at a low cathodic potential. The respective peak of the current transient is used to monitor the relative changes of the anodic oxides. The results are discussed from the point of view of non-radiative defect generation during electropolishing, which is controlled by the potential and the rate of oxidation.

Introduction

The silicon/fluoride electrolyte system has been extensively studied in the past years. A current transient at the end of the dissolution of an oxide-covered silicon electrode in fluoride solutions could be observed [1 – 4]. The achievement of the current maximum depends on the etchrate of the solution and the thickness of the oxide [2, 5]. At the current maximum the etching front reaches the interface and leads to a hydrogenation of the Si-surface [4, 5]. Electropolishing with current oscillations followed by hydrogenation produces smooth and electrically well passivated Si-surfaces [6, 7]. The physico-chemical origin of the current oscillations, which occur in a narrow anodic potential regime, is still under discussion [2, 3, 8 – 15]. Changes in surface morphology [10 – 14], hole formation [12 – 14] and variation of the amount of oxide [12 – 15] have been obtained by the oscillatory behavior of the current.

We use in-situ photoluminescence (PL) measurements to investigate the PL quenching, induced by non-radiative recombination centers, at the semiconductor/electrolyte interface during current oscillations on p-type Si(100).

Experimental

P-type Si(100) samples with a specific resistivity of about 1 Ω cm are used in the experiments. The samples are pretreated in $HNO_3 : H_2O_2 : H_2O$ (1:1:6) for 5 min. The resulting oxide is then etched back in 1 M NH_4F (pH 4.0) for 1 min. The Si sample, which serves as working electrode, is contacted with In/Ga and silver epoxy. Pt wire and 1 M $KCl/AgCl/Ag$ are used as counter and reference electrode, respectively. The Si-samples are placed at the center of a quartz tube. The electrolyte is continuously pumped through the quartz tube during the experiments. The elec-trode current or potential was controlled by a galvanostat/ potentiostat (Jaissle IMP 88 PC). The electrolyte (0.1 M NH_4F, pH 4.2) is made from p.a. NH_4F, triply distilled water and H_2SO_4 for pH adjustment. The PL is excited by a N_2-laser (wavelength 337 nm, pulse width 0.5 ns). The light intensity is about 0.5 mJ/cm². The estimated heating is below 3 K during some ns after illumination. The PL transients are detected at a wavelength of 1.05 μm using a prism monochromator, a Si-photodiode with a high impedance preamplifier (EMM) and a digital oscilloscope (HP 54510 A). The experiments are started from the hydrogenated Si-surface monitored by leveling out of the current transient at −0.45 V. It should be remarked that both, hydrogenation [4, 5] and electrical passivation [7], are completed after the transient has been decayed.

Results

(a) Dependence of the PL Intensity on the Anodic Potential and Current During Electropolishing

Fig. 1 shows a typical current voltage curve of p-type Si(100) in the acidic aqueous fluoride solution starting from the hydrogenated surface at −1 V. With increasing potential the current suddenly increases up to a current peak at which oxide formation sets on [15]. The oxide formation is accompanied by the simultaneous etch-back of the oxide by the acidic fluoride solution resulting in the well-known electropolishing behavior. Current oscillations occur in the potential region from about +5 V to less than +12 V and are damped at higher potentials. Fig. 2 shows the current-time and PL-time behavior of the p-Si(100) surface during electropolishing at +3.5 V (■, ●) and +12 V (□, ○). In both cases the current densities and PL signals are nearly constant over a long period (the rest of one strongly damped oscillation can be seen at +12 V). The mean current is practically equal at both potentials while the PL-signal at +12 V is about 10 times higher. It can be concluded that the PL intensity depends on the applied anodic potential during electropolishing.
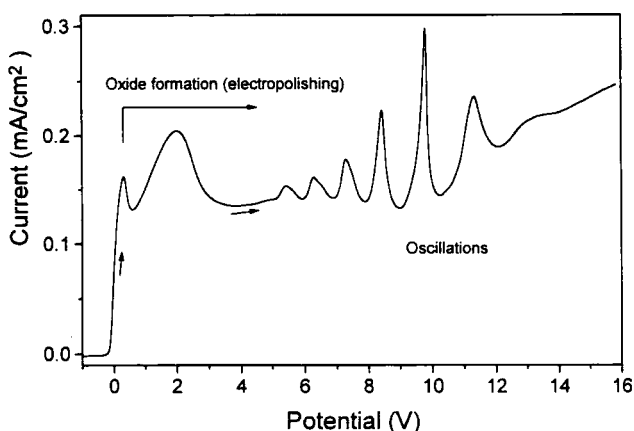

Fig. 1
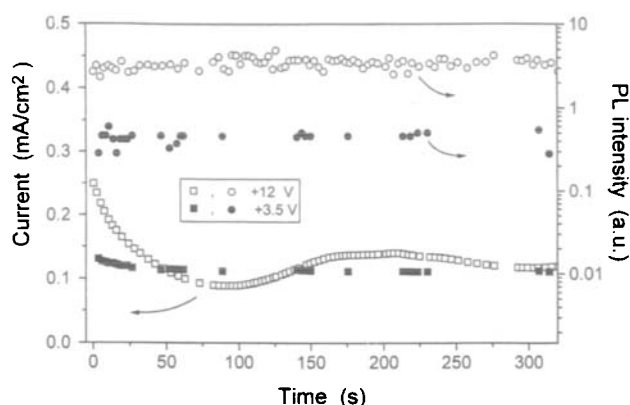Current-potential dependence of p-Si(100) in 0.1 M NH_4F (pH 4.2); scanrate 20 mV/s

Fig. 2
Current and PL as a function of time at +3.5 V and +12 V, respectively

Fig. 4
Maximum and minimum PL intensity during electropolishing as a function of the applied potential

The current-time and PL-time behavior in the oscillating regime at +10 V is plotted in Fig. 3. The current increases heavily just after switching on the potential. The first oscillations consist of broad and asymmetric peaks. The current peaks become more and more uniform and symmetric with increasing time, and the PL signal oscillates with the same period. When the current peak gets sharper and higher in amplitude, the oscillation of the PL intensity is also sharpened and reaches very low values. Furthermore, an anticorrelation is observed between the oscillation of the current and the PL intensity. This gives evidence for the influence of the oxidation rate on the PL quenching, especially as the oxidation rate is characterized by the current density at a fixed potential.
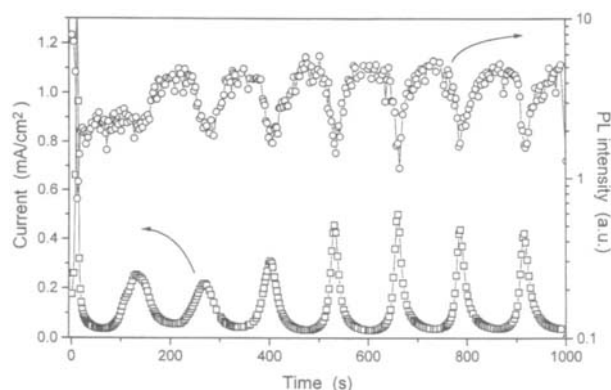

Fig. 3
Current and PL as a function of time at +10 V

Fig. 4 shows the maximum and minimum PL signal during the oxidation process as a function of the anodic potential. The minimum PL signal increases with increasing potential and tends to saturate at higher anodic potentials where no current oscillations could be observed (above +11 V in our case). The maximum PL signal increases also with increasing potential and reaches the largest value at about +10 V. This demonstrates that the Si surface passivation can be optimized even for electropolishing in the oscillating regim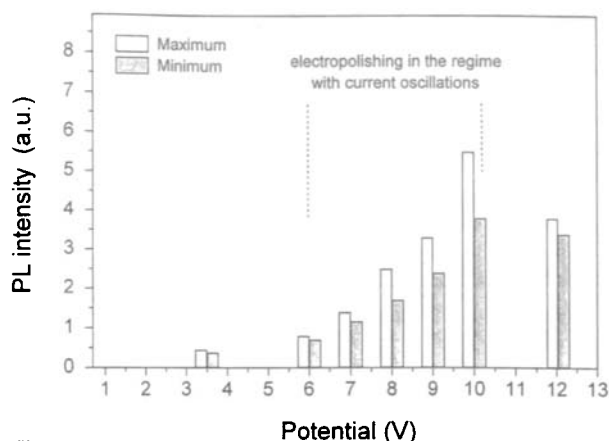e. It should be remarked that such effects could not be observed by conventional capacitance voltage [17] or surface photovoltage [7] measurements. These techniques are not applicable for in-situ monitoring of changes even at anodic oxide/c-Si interfaces since the trap and charge density in wet anodic oxides is very high.

(b) Oxide Removal – Investigation of the Current Transients

As shown in part (a) the PL intensity is a function of the applied potential and the current, and is specifically pronounced during the oscillations. The relative change of the thickness of the very thin anodic oxide layers can be investigated by using the current transient peaks as a monitor for the complete oxide removal [2, 4, 5]. This is quite reasonable since the development of surface hydrogenation and passivation starts even just after the current transient reaches his maximum and tends to decay [5, 7]. Fig. 5 shows the semilogarithmic plot of the current transient after switching the potential from the oxidation state to −0.45 V in the same solution. The time base is scaled to the interruption of the current after switching the potential from anodic
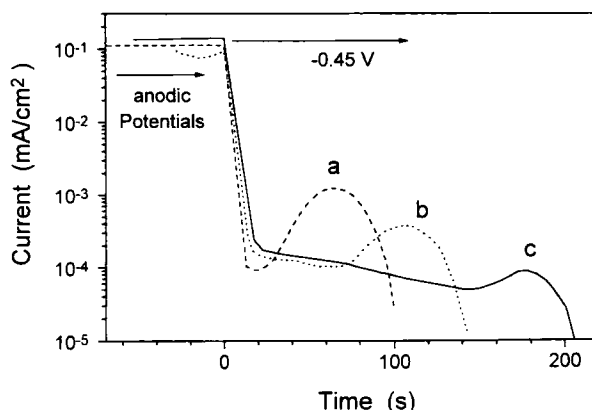

Fig. 5
Current-transients at −0.45 V after different anodic potentials (a, b, c: +3.5 V, +9 V, +12 V)

to slightly cathodic. With increasing oxidation potential (+3.5 V, +9 V, +12 V; Fig. 3a,b and c, respectively) the onset of the current peak, t_{peak}, appears at a later time due to an increased oxide thickness. Further, it can be seen that the current transient decreases with increasing preceding anodic potential. The values of the oscillation period, t_{osc}, and of t_{peak} are compared in Fig. 6 as a function of the anodic potential during electropolishing. Both t_{osc} ($\square$) and t_{peak} ($\blacksquare$) increase linear with increasing potential which reflects to a proportional dependence of the oxide thickness on potential [2]. The values of t_{osc} and t_{peak} are very similar but not equal, t_{osc} is about 6 s below t_{peak}. It can be concluded that the anodic oxide with maximal thickness is not completely etched back during the period of one oscillation. This agrees with IR measurements which did not show the formation of a partially hydrogenated Si surface during the oscillations [14, 15]. Furthermore, Fig. 6 represents also data of oscillation periods from other authors using similar solution composition for n-Si(111) ($\triangle$, $\blacktriangle$: 0.1 M NH$_4$F; pH 4) [2] and p-Si(100) ($\bigcirc$: 0.1 M NH$_4$F; pH 3.8) [12]. The values of t_{osc} from these experiments are below t_{osc} obtained in our work due to the higher etchrates of their solutions.

Fig. 7

Dependence of the integrated electric charge of the current transient, Q_t, on the applied potential during the preceding electropolishing. The inset illustrates the determination of Q_t
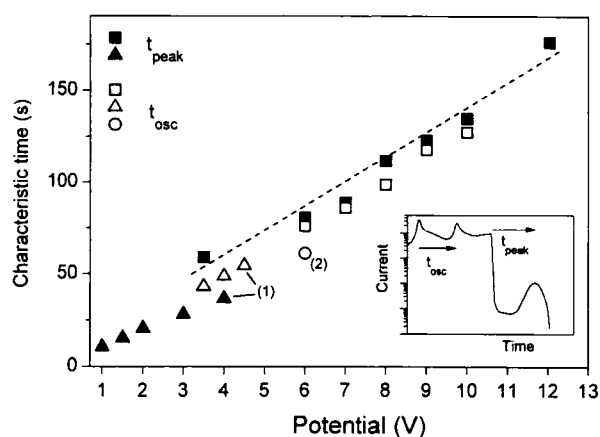

Fig. 6

Dependence of the characteristic times t_{osc} (oscillation period) and t_{peak} (time of the current transient maximum after switching the potential to −0.45 V) on the applied anodic potential during electropolishing. Values (1) and (2) are from Ref. 2: n-Si(111) ($\triangle$, $\blacktriangle$: 0.1 M NH$_4$F; pH 4) and Ref. 12: p-Si(100) ($\bigcirc$: 0.1 M NH$_4$F; pH 3.8). The inset illustrates the determination of t_{osc} and t_{peak}

Fig. 7 shows the dependence of the integrated electric charge of the current transient at −0.45 V, Q_t, on the applied potential. The inset illustrates the determination of Q_t which decreases with increasing potential. Earlier experiments concerning the electric charge were carried out at n-type silicon by switching off the light and holding the Si-electrode at the respective oxidation potential [2]. But a higher anodic potential in the dark leads to an increase of the current transient with respect to a lower anodic polarisation [14] and therefore to an increase of the electric charge. Consequently, the authors in Ref. 2 did not see any changes
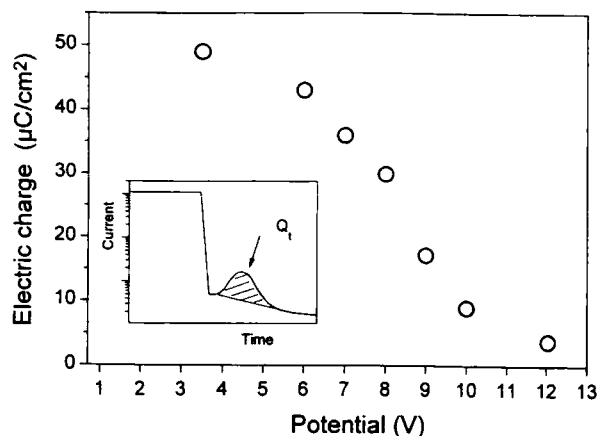
in the charge during the current transient. Therefore, we measured the current transients always at a fixed potential of −0.45 V which allows a comparison of the measured charge.

Another interesting point of our investigation concerns the homogeneity of the thin anodic oxide during the current oscillations. Fig. 8 shows the current transients at −0.45 V after electropolishing at +8 V and interruption in the oscillation maximum (thick solid line) and minimum (thin solid line). The dotted line shows the difference of both. Interruption at the maximum leads to a broadening of the current peak into the direction of earlier times. Therefore, the thickness of the anodic oxide is much more homogeneous at the minimum. The difference of the transients is very similar to the current transient obtained at +6 V. This finding suggests that there are mainly two different thicknesses of the anodic oxide.

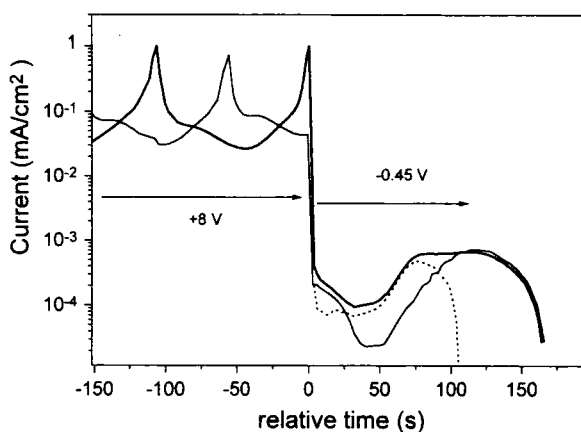
Fig. 8

Current-transients at −0.45 V after electropolishing at +8 V and interruption at the maximum (thick solid line) or the minimum (thin solid line) of an oscillation. The dotted line shows the difference of both

Discussion

The measured PL intensity of the crystalline bulk silicon is controlled by the non-radiative recombination in the bulk and at the c-Si/oxide interface. The bulk recombination is unchanged during the low temperature electrochemical treatments. So, the PL quenching in our experiments is related to the concentration of non-radiative defects at the Si surface. The defect concentration depends on the structure of the interface region between the Si bulk and the thin anodic oxide, which is controlled by the applied potential and by the oxidation rate at a fixed potential. Our experimental findings show that the non-radiative recombination, i.e. the defect concentration at the Si surface, decreases with increasing potential and anticorrelates with the oxidation rate during electropolishing which is monitored by the current at a constant potential. Further, the oxide thickness increases and the integrated electric charge of the current transient decreases with increasing anodic potential. Regarding to Gerischer et al. [2] the anodic current transient is probably related to the oxidation of not fully oxidized Si atoms at the Si surface. That means, the lower Q_t the lower the concentration of defective Si atoms at the Si surface. This is confirmed by our in-situ PL measurements. It should be remarked that the Si atoms with both, silicon or oxygen, backbonds may be not directly the non-radiative surface recombination centers, but they are related to the defect generation such as dangling bonds during the oxidation process. At present it is not completely clarified what kind of defects are induced by the electrochemical treatment and which of them are PL active. We think that the anticorrelation between the PL intensity and the current oscillation is a result of the high rate of oxide formation during the increase of the current density. Obviously, this high rate leads to the formation of disordered and possibly not fully oxidized Si-atoms in the SiO_2 layer as proposed by Gerischer et al. [2]. The current oscillations are induced by nonuniform anodic oxidation leading to a periodically change in oxide thickness [12, 13]. The oxidation rate determines the cracking of Si-backbonds and the formation of dangling bonds as the initial step of oxidation. These dangling bonds are quickly passivated by oxidizing species and free radicals in the electrolyte. It is known that dangling bonds at Si-atoms with three Si-backbonds, that means the dangling bonds closest to the bulk silicon, are very efficient non-radiative recombination centers [16].

Regarding the time difference of $t_{peak} - t_{osc}$ (6 s) the minimal thickness of the anodic oxide is in the order of the tunneling length of carriers from the Si surface into the electrolyte. This confirms the model that formation of holes in the anodic oxide triggers the oscillations [12, 13]. We assume that the observed time difference of about 6 s corresponds to a thin tunneling oxide which must exist in the holes of the oxide layer until the current and the oxide thickness increases. Taking into account that tunneling oxides have a thickness in the order of 3 ML SiO_2 (10 Å), the oxide thickness during oscillations at $+8$ V (see Fig. 8) varies about 35%, mimimum (135 Å) to maximum

(180 Å). This is in good agreement with in-situ FTIR [14] and in-situ ellipsometric [18] investigations during photocurrent oscullations at $+6$ V at n-Si(111) in a similar solution. The oxide thickness (100 to 150 Å) and the amount of SiO_2 change by about 50%. The oxide is most inhomogeneous at the current maximum which is well correlated to the PL minimum.

Conclusions

In-situ PL measurements are applied for the characterization of the p-type Si(100) surface during electropolishing. The concentration of non-radiative defects decreases with increasing potential and decreasing oxidation rate at a fixed potential. If current oscillations occur, the PL intensity oscillates with the same period. The thickness of the thin anodic oxide is most inhomogeneous at the maximum of the current oscillation where the PL intensity reaches the minimum. The occurrence of the current transient after the removal of the thin anodic oxide layer can be used as a monitor for the oxide thickness and for the quality of the c-Si/anodic oxide interface.

References

[1] M. Matsumura and S. R. Morrison, J. Electrochem. Soc. 147, 157 (1983).
[2] H. Gerischer and M. Lübke, Ber. Bunsenges. Phys. Chem. 92, 573 (1988).
[3] F. Ozanam, J.-N. Chazaviel, A. Radi, and M. Etman, Ber. Bunsenges. Phys. Chem. 95, 98 (1991).
[4] T. Bitzer, M. Gruyters, H.J. Lewerenz, and K. Jacobi, Appl. Phys. Lett. 63, 397 (1993).
[5] J. Rappich and H.J. Lewerenz, J. Electrochem. Soc. 142, 1234 (1995).
[6] S. Rauscher, Th. Dittrich, M. Aggour, J. Rappich, H. Flietner, and H.J. Lewerenz, Appl. Phys. Lett. 66, 3018 (1995).
[7] Th. Dittrich, S. Rauscher, T. Bitzer, M. Aggour, H. Flietner, and H.J. Lewerenz, J. Electrochem. Soc. 142, 2411 (1995).
[8] D.R. Turner, J. Electrochem. Soc. 105, 402 (1958).
[9] M. Etman, M. Neumann-Spallart, J.-N. Chazalviel, and F. Ozanam, J. Electroanal. Chem. 301, 259 (1991).
[10] H.J. Lewerenz and G. Schlichthörl, J. Electroanal. Chem. 327, 85 (1992).
[11] J. Rappich, H. Jungblut, M. Aggour, and H.J. Lewerenz, J. Electrochem. Soc. 141, L99 (1994).
[12] H.J. Lewerenz and M. Aggour, J. Electroanal. Chem. 351, 159 (1993).
[13] M. Aggour, M. Giersig, and H.J. Lewerenz, J. Electroanal. Chem. 383, 67 (1995).
[14] J. Rappich, M. Aggour, S. Rauscher, H. Jungblut, and H.J. Lewerenz, Surf. Sci. 335, 160 (1995).
[15] F. Ozanam and J.-N. Chazalviel, J. Electron Spectrosc. Relat. Phenom. 64/65, 395 (1993).
[16] H. Flietner, Proc. 7th Conf. Insulating Films on Semiconductors (INFOS) pp. 151 – 154, ed. by W. Eccleston and M. Uren, Hilger, Bristol 1991 and references therein.
[17] G. Oskam, P.M. Hoffmann, and P.C. Searson, Phys. Rev. Lett. 76, 1521 (1996).
[18] M. Aggour, Dissertation, TU Berlin (1994).