JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 1179–1183

An improved electrochemical cell for the characterization of silicon/electrolyte interfaces

V. BERTAGNA

Laboratoire d'Analyses IBM, 91105 Corbeil Essonnes, France

F. ROUELLE, M. CHEMLA*

Laboratoire d'Electrochimie. Université Pierre et Marie Curie, 75005, Paris, France

Received 1 November 1996; revised 2 January 1997

An electrochemical cell was made of a Teflon tube which was tightly pressed on the surface of a silicon wafer. The Teflon/silicon contact was tight enough to prevent any infiltration of solution, because it was observed that confined electrolyte was a source of irreproducibility. The device was enclosed within a black polyvinyl box which protected the sample against room light but allowed irradiation with a controlled light intensity. The cell was fed under argon pressure with a thoroughly degassed electrolyte, and the whole volume inside was maintained under argon atmosphere. This cell permitted very stable and reliable rest potential measurement and current–potential diagrams. The method proved useful in the study of the influence of light irradiation and of dissolved oxygen or metal ions trace impurities in the electrolyte.

Keywords: *Silicon–electrolyte interface, Silicon surface characteristics, Semiconductor surface defects, Surface potential measurements*

1. Introduction

Ultralarge-scale integrated (ULSI) devices are becoming increasingly integrated, at the scale of subhalf micrometre geometry, to increase their density and rapidity. In this context, very high levels of silicon wafer cleanliness and surface structure are required for better reliability and performance [1–3]. Although other techniques, such as plasma etching processes, have been developed, the wet process, using dilute HF (DHF) solutions, is still employed extensively to clean Si surfaces, mainly because it can be used at room temperature and does not damage the wafers [4–6]. In fact, most authors recognize that, upon treatment by DHF, pure silicon surfaces are protected by Si–H terminal bonds which generate a passive layer [7]. A perfect monitoring of wafer/liquid interfaces is essential to further advance process technology.

Several new techniques have been introduced to control metallic contamination and microroughness of the silicon wafer surface with a high sensitivity. The most harmful surface defects are particulate contaminants, metallic impurities, organic compounds, native oxide, microroughness and adsorbed molecules. The commonly used techniques are the total reflection X-ray fluorescence (TXRF) [8], atomic force microscopy (AFM) and scanning tunnel microscopy (STM). Electrochemical studies often consist in voltammetric measurements which lie in a rather wide interval of potential [9]; these procedures lead to a serious etching of the surface and to the formation of porous silicon [10]. Some recent works used a more restricted range of potential, about 1 V, to elucidate the mechanism of silicon anodic dissolution [11].

The aim of the present work is to develop electrochemical techniques to characterize the behaviour of silicon surfaces in contact with DHF, the applied potential being very close to the rest potential, and to determine the parameters which control the kinetics of the electrochemical reactions coupled to the electron transfer at the interface. The most important parameters for the characterization of the silicon/electrolyte interface are: (i) the open circuit potential, E_r, at zero current which determines the relative reactivity of anodic and cathodic sites; (ii) the polarization resistance, R_p, which leads to the corrosion current i_{corr} expressed in $\mu A\,cm^{-2}$ or in number of atoms dissolved per unit time; and (iii) the voltammetric diagram which can give information about the mechanisms involved in anodic and cathodic electrochemical reactions. In this case, the range of scanned potential should be restricted to a narrow interval, say $\pm 250\,mV$, around E_r to prevent any excessive change of the surface roughness.

2. Experimental details

In a series of preliminary experiments, we used an electrochemical cell as described recently [12], this cell

---

*Author to whom correspondence should be addressed.

0021-891X

being usually encountered in electrochemical studies on silicon materials [13, 14]. In this device, the silicon wafer was in contact with the HF electrolyte contained in a polymer vessel by means of an O-ring seal. However, the first measurements of open circuit voltage were not reproducible within a few 100 mV range, as already pointed out by Föll [15]. A deep analysis of the results leads us to believe that the experiments were subject to many factors of irreproducibility such as:

(i) The presence of dissolved oxygen in variable concentration.
(ii) The diffusion of photons from room light into the cell.
(iii) The contamination of the electrolyte solution at the ppb level by metal ion traces or by adsorbable organic molecules.
(iv) The presence of metal impurities or roughness at the surface of the wafer.
(v) Finally, we must point out that a very thin layer of electrolyte can infiltrate between the O-ring and the silicon sample. This erratic phenomenon was very often observed although the silicon surface was hydrophobic, despite the high pressure exerted on the seal and whatever was the constituting material. The formation of this thin layer of confined liquid results in a perturbation of the measured potential which can reach a few 100 mV.

To satisfy all the requirements necessary to obtain reproducible and reliable electrochemical parameters, a new electrochemical cell (Figs 1 and 2) has been designed with special features, in addition to a specific experimental procedure, which permitted the surface potential to be measured with a good precision (±20 mV), the experiments being carried out at 20 °C.

The electrochemical cell itself (Fig. 1) is mainly constituted of a Teflon tube, 2 cm interior diameter, which is applied on the silicon surface with a watertight contact. To achieve a perfectly waterproof contact, the bottom surface of the Teflon tube is finely polished with a diamond suspension 0.1 μm, and strongly pressed onto the silicon wafer between two black polyvinyl plates using four screws. This cell was protected against room light by a box made of black polyvinyl. As Figure 1 shows, the two plates keeping the silicon sample in a horizontal position prevent external light reaching the sample. Moreover, a mask made of a black plastic sheet surrounds the polyvinyl support. On the other hand, a hole on the top cover allows the irradiation by means of an optical fibre device, to study the influence of a controlled light source, 1400 lux intensity. The advantage of such a cell is the small volume of electrolyte, 10 ml, needed to record electrochemical measurements.

Figure 2 shows the device designed for the preparation and feeding of the electrolyte solution. It is constituted of an airtight polyethylene container filled with the liquid and fitted with two Teflon tubings whose function depend on the setting of the four ways valve: (i) in the configuration presented (Fig. 2), the argon gas (N60 grade, containing less than 1 ppm residual O_2) bubbles through the solution, and is then transferred into the electrochemical cell and creates the required inert atmosphere. (ii) When the valve is rotated of a $\pi/2$ angle, the argon gas is introduced above the liquid level and gives rise to an excess pressure which then carries the deaerated solution through the tubing into the cell. At the beginning of a

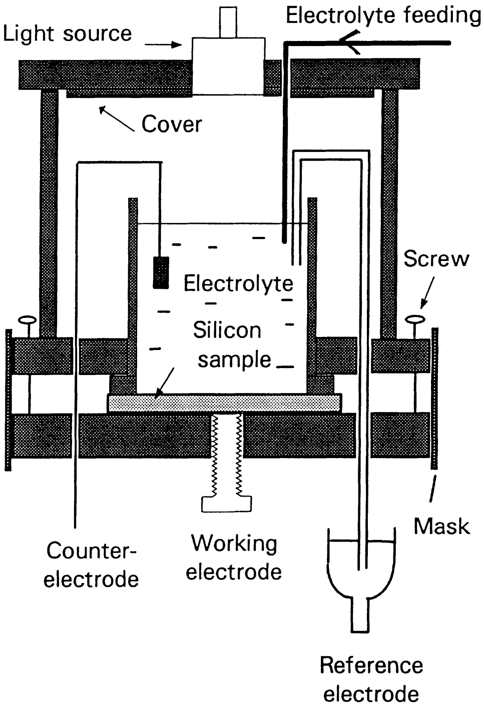

Fig. 1. Electrochemical cell design for the characterization of silicon wafer surfaces.

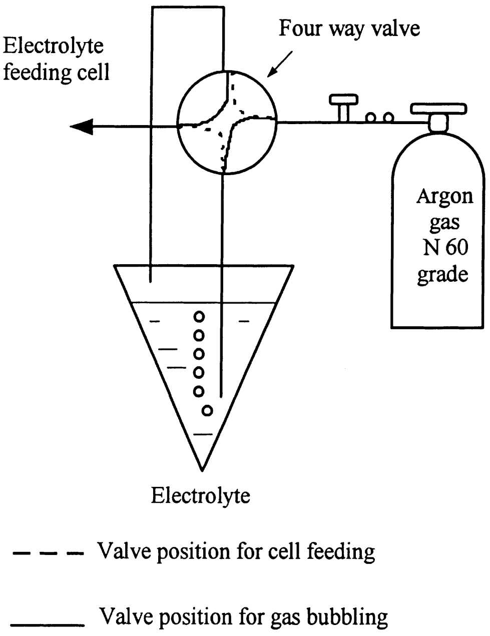

Fig. 2. Device for the preparation and feeding of the electrolyte solution.

run, the electrolyte in the container is thoroughly outgassed by argon bubbling for at least 1–2 h. The volume of solution inside the electrochemical cell is $10\,cm^3$; the volume of the electrolyte reserve in the container is $150\,cm^3$. The tubings are made of Mylar which minimizes the pollution of Argon by air back diffusion. This experimental scheme allows a precise and quantitative comparison of the electrochemical properties of silicon in contact with DHF solutions under various conditions: for example in the dark or with light irradiation, with pure deoxygenated or with oxygen saturated DHF, and influence of metal ion impurities in solution at the level of trace amounts.

The electrolyte, DHF 5%, was prepared from a 40% SLSI grade (sublarge–scale integration) HF solution, containing less than 1 ppb metallic impurities, using high purity deionized water produced in the IBM facilities site. Silicon wafers, n and p type (125 mm dia. × 625 μm thick) were purchased from MEMC electronic materials:

p type: boron doped at the level 1×10^{15} at. cm^{-3}
p type: boron doped at the level 5×10^{16} at. cm^{-3}
n type: phosphorus doped at the level 2×10^{14} at. cm^{-3}
n type: phosphorus doped at the level 2×10^{16} at. cm^{-3}

These wafers were CZ (1 0 0) oriented, with one face mirror polished for CMOS applications, and the backside was mechanically polished to enhance gettering which facilitates the treatment to establish an ohmic contact.

In our experiments the silicon samples were beforehand cleaned with a mixture of H_2SO_4:H_2O_2 (3:2) at 80 °C for 10 min to oxidize surface impurities and grow a new SiO_2 layer. The sample is then thoroughly rinsed with deionized water and then cleaned by a DHF solution to promote a pure silicon surface passivated by Si–H_x termination bonds.

As the input impedance of the potentiostat is more than 10^{10}, the electrical contact on the back side of the silicon wafer could be simply obtained with a thin gold plate pressed on the surface. The contact resistance of the interface Au/Si was found to be less than 100 Ω. However, careful electrochemical measurements require a backside sample pretreatment, in order to obtain a negligible interface electrical resistance. The silicon reverse side is at first deoxidized by gently rubbing the surface with a small cotton tip imbued with DHF solution, and then covered a Ga–In alloy which penetrates the silicon lattice and promotes an ohmic contact for the charge carriers flow. A gold foil is inserted between the Ga–In layer and the screw connected to the potentiostat. Thus we obtained a purely ohmic contact whose resistance value was equal to a few ohms, which is negligible in the case of the determination of the polarization resistance, the current being then less than 1 μA. Rest potential values were referred to the saturated calomel electrode (SCE). The calomel electrode is connected to the electrolyte by means of a bridge made of a teflon capillary tube filled with a KCl jellied solution. The counter-electrode was a platinum plate.

Electrochemical parameters were measured by means of a Tacussel Radiometer Analytical PGS 201T potentiostat. This device was driven by an IBM PC computer using Voltamaster software, which includes several electrochemical programs such as chronopotentiometry, polarization resistance, linear and cyclic voltammetry. For each run, numerical data were recorded in files which were also used as well for drawing the corresponding graphs, and for mathematical treatment leading to the validation of an interpretative model.

3. Results

This cell coupled with this experimental method, leads to values of rest potential, E_r, which is stable versus time and reproducible. Figure 3 represents the recorded value of the rest potential of a p-type silicon, doped 1×10^{15} at. cm^{-3}, in deaerated DHF, in the dark and under illumination by a 1400 lux photon flux. It is interesting to note that the illumination induces a highly positive photopotential $\Delta E \simeq +480\,mV$. This result supports the interpretation of the open circuit potential in terms of electrochemical processes. In fact, it is interpreted by the generation of electron-hole generation with light which strongly increases the relative concentration of minority carriers. In the case of p-type silicon, the increase of electron carriers contributes to promote the reduction reaction of protons and to shift the mixed potential towards positive values. In the case of n-type silicon the observed photopotential was negative as a consequence of the generation of h^+ minority carriers which promote the oxidation of Si atoms. Such results are in close agreement with photocurrent measurements on n–Si by Kucernak *et al.* [16], and on p–Si by Schlichthörl *et al.* [17].

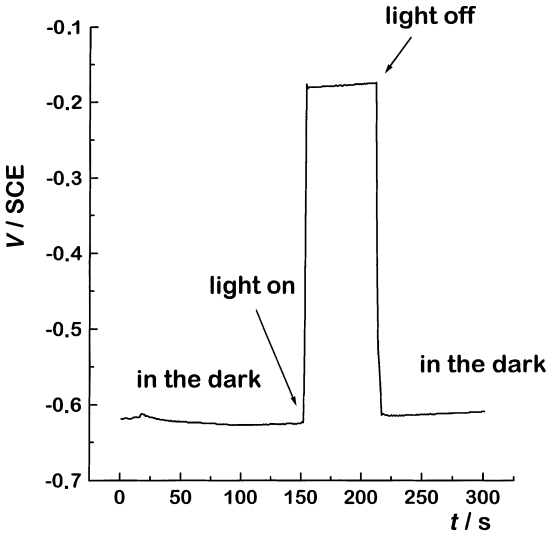

Fig. 3. Recorded values of the rest potential of p-type silicon in carefully deaerated HF solution, in the dark and under illumination.

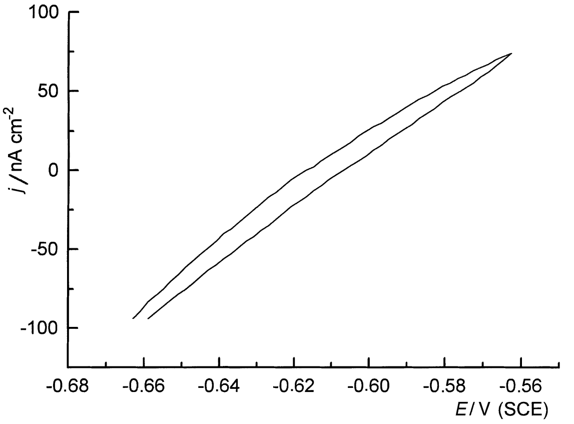

Fig. 4. Determination of R_p by voltammetry, in a narrow range of potential, of p-type silicon in carefully deaerated HF solution.

On the other hand, scanning the potential within a narrow range (±50 mV around the rest potential) gives a voltammetric response useful for the determination of the polarization resistance R_p with negligible surface tarnishing. Figure 4 represents the current–potential curve leading to the polarization resistance of the same sample, in the dark.

From the theoretical treatment of the mixed potential involving the kinetics of electrochemical reactions, the slope of the current–voltage curve near zero current is equal to R_p, which is related to the corrosion current i_{corr}:

$$(dE/di)_{i=0} = R_p = RT/(\alpha + \beta)nF\, i_{corr} \qquad (1)$$

Thus, this measurement allows the determination of the dissolution rate (dN/dt) per unit of surface and time. In this equation the term $(\alpha + \beta)$ is assumed to be nearly equal to 1, and the reaction valence n is set equal to 2 in agreement with published results [17] indicating that, at low current density, the anodic oxidation of Si is an EC mechanism, the kinetics being controlled by an electrochemical step with a two-electron transfer.

$$dN/dt = i_{corr}\, N_A/2F \qquad (2)$$

where N_A is the Avogadro number and dN/dt is in atoms cm^{-2} s^{-1}.

As an example, the data shown in Table 1, E_r , R_p and dN/dt, were obtained with n and p doped silicon samples, in oxygen free 5% DHF, at 20 °C, in the dark.

It is difficult to predict a rigorous relationship between the corrosion rate and the doping level, since, depending on the substrate stock, the corrosion rate is highly sensitive to surface imperfections. The remarkable reproducibility and stability of the open circuit potential obtained with this device permitted to demonstrate the influence of electrolyte confinement over a part of the wafer area. Figure 5 illustrates an example of the potential variation when the silicon surface is covered by a piece of insulating material resulting in the confinement of a thin film of solution in between. In this experiment, the n-type silicon sample was maintained in the cell, filled with deaerated DHF solution during the first 2 min in order to record its free potential and to check its stability. After this time, a Teflon plate disc was pressed on the silicon surface near the central part of the sample. A sudden rise of the potential more than 150 mV was then observed. At present, this change in the electrochemical parameters is considered as a detrimental effect which could be responsible for erratic results.

However, the interpretation of this effect is only qualitative. It is possible that, owing to the high purity of the Si wafers, the exchange current is less than 1 μA cm^{-2}, and then a very small variation of the reactivity of anodic or cathodic sites will result in a steep change in the open circuit voltage.

Finally, this electrochemical cell also proved very efficient for the detection of contaminants in the electrolyte solution as well as on the semiconductor surface. Figure 6 demonstrates the gradual variation of potential of a n–Si sample when the DHF solution is contaminated by 100 ppb and 300 ppb Cu^{2+} ions, respectively. The increment of rest potential was observed to be positive, for both p-type and n-type sil-

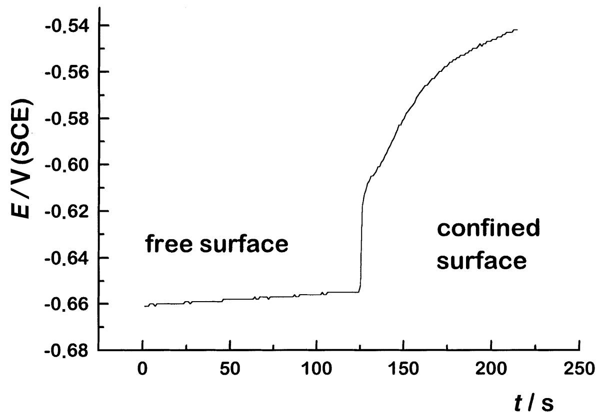

Fig. 5. Open circuit potential of a n-type potential in deoxygenated DHF solution, and observation of the confinement effect.

Table 1. Electrochemical parameters for p and n-type silicon contacting a deoxygenated DHF solution, in the dark

	p–Si 1 × 10^{15} at. cm^{-3}	*p–Si* 5 × 10^{16} at. cm^{-3}	*n–Si* 2 × 10^{14} at. cm^{-3}	*n–Si* 2 × 10^{16} at. cm^{-3}
E_r /V/ECS	−0.65 ±0.04	−0.641 ±0.012	−0.653 ±0.03	−0.708 ±0.03
R_p/Ω cm^2	557 800	1 033 000	253 000	156 500
dN/dt/at. cm^{-2} s^{-1}	7.05 × 10^{10}	3.8 × 10^{10}	1.6 × 10^{11}	2.6 × 10^{11}

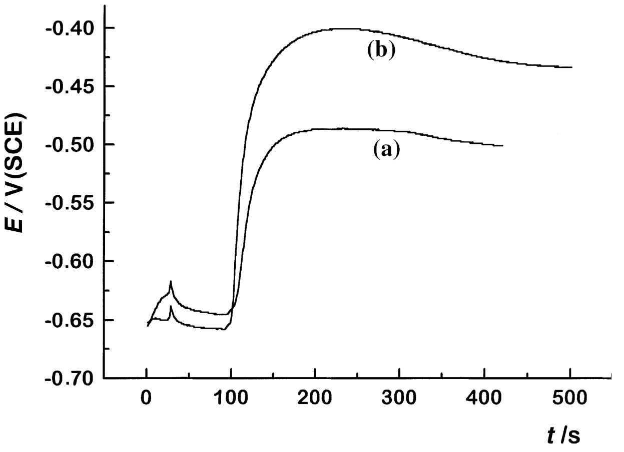

Fig. 6. Recorded values of rest potential of n-type silicon when Cu^{2+} contaminant is added to the HF solution. Contaminant concentration upon addition: (a) 100 ppb and (b) 300 ppb.

icon. Indeed, this gradual variation reflects the deposition kinetics of copper micronuclei, nonpassivated, which act as cathodic sites for proton electron transfer, and then contribute to shift the rest potential towards more positive values. The method proved to be very sensitive to the presence of metal impurities, at the level of a few ppb, in the HF solution. Moreover, a silicon surface already contaminated with metal impurities, although in contact with very pure DHF solution, was characterized by a net alteration of the rest potential which was more positive, together with a sharp decrease in the polarization resistance.

4. Conclusion

We conclude that this electrochemical technique is a very efficient tool, sensitive for the detection of surface defects on semiconductor materials and ionic impurities in electrolyte solutions.

The experimental cell and procedure allow very reproducible surface potential measurements (± 20 mV) for samples belonging to the same stock, whereas uncertainty reaches ± 100 or 200 mV in any previously designed cell.

This, in turn, allows use of the cell to characterize the surface properties of silicon wafers in the course of normal processing. The potential applications for online process control are great: *viz.* (i) characterization of surface states after cleaning, after implant, vacuum treatment, plasma exposure etc. and (ii) characterization of chemical solutions (contamination of DHF solutions).

Finally, this method is potentially useful for the study of the surface properties of any metal, as well as the protecting power of coatings on metals, and also the measurement of the residual resistance of an insulating layer.

Acknowledgements

The authors express their thanks to Dr C. Plougonven, IBM Company, for fruitful discussions, and to MEMC Company for providing n and p-doped silicon wafers.

References

[1] G. Zoth and W. Bergholz, *J. Appl. Phys.* **67** (1990) 6764.
[2] R. R. Kola, G. A. Rozgonyi, J. Li, T. Y. Tan, K. E. Bean and K. Lindberg, *Appl. Phys. Lett.* **55** (1989) 2108.
[3] W. Henley, L. Jastrzebski and N. Haddad, *in* Proceedings of the 1993 IEEE International Reliability Physics Symposium (1993), p. 22.
[4] W. Kern, *J. Electrochem. Soc.* **137** (1990) 1887.
[5] T. Ohmi, *ibid.* **140** (1993) 811.
[6] K. Ljungberg, Y. Bäcklund and A. Söderbärg, *ibid.* **142** (1995) 1299.
[7] Y. J. Chabal, G. S. Higashi, K. Ragavachari and V. A. Burrows, *J. Vac. Technol.* **A7** (1989) 2104.
[8] L. Torcheux, Thesis, University Paris VII (1994).
[9] C. Levy-Clement, A. Lagoubi, R. Tenne and M. Neuman-Spallart, *Electrochim. Acta* **37** (1992) 877.
[10] I. Ronga, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon and F. Muller, *J. Electrochem. Soc.* **138** (1991) 1403.
[11] X. G. Zhang, S. D. Collins and R. L. Smith, *ibid.* **136** (1989) 1561.
[12] L. Torcheux, A. Mayeux and M. Chemla, *ibid.* **142** (1995) 2037.
[13] S. A. Hendricks, Y. T. Kim and A. J. Bard *ibid.* **139** (1992) 2818.
[14] H. D. Lee, H. J. Lee, C. K. Kim and C. H. Han, *Appl. Phys. Lett.* **66** (1995) 3272.
[15] H. Föll, *Appl. Phys. A, Solids Surf.* **53** (1991) 8.
[16] A. R. Kucernak, R. Peat and D. E. Williams, *ibid.* **138** (1991) 1645.
[17] G. Schlichtörl, E.A. Ponomarev and L.M. Peter, *ibid.* **142** (1995) 3062.
[18] R. Memming and G. Schwandt, *Surf. Sci.* **4** (1966) 109.