Copper Contamination Mechanism of Silicon Substrates from HF Solutions

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The contamination of silicon wafers from dilute HF solutions containing ultratrace levels of metallic ion impurities is a subject of constant interest. The mechanism of copper electroless deposition from HF onto monocrystalline silicon was investigated using a new electrochemical cell, which proved to be a very sensitive detector for in situ characterization of silicon surfaces.

Upon addition of copper trace amounts, the open-circuit potential was observed to shift rapidly towards more positive values at a rate nearly proportional to the copper concentration. All potential/time curves tend to reach a limiting value of the potential, while quantitative measurements of radioactive tracers revealed that during a few tens of minutes, copper ions were continuously reduced on the silicon surface.

Electrochemical potentials and voltammetric measurements were interpreted in terms of the mixed potential theory and led to the conclusion that copper nuclei act as a catalyst which enhances the cathodic activity for protons reduction. The model was supported by AFM observations which demonstrated the initiation of corrosion pits around the nuclei.

Key words: Silicon, contamination, copper, catalysis.

Introduction

As the dimensions of semiconductor devices are downsized, aiming at manufacturing VLSI and ULSI circuits, the cleaning of the silicon surfaces is one of the most critical operations in the fabrication of integrated circuits. The gate oxide electrical characteristics being very sensitive to contaminants, it is essential to study the contamination of Si wafers together with the resulting corrosion process occurring during wet treatment. [1 - 4].

Indeed, inorganic particles, metallic clusters in the range of 10^{12} atoms/cm^2, and adsorbed organic compounds severely affect the electrical performance of devices by reducing the carrier-lifetime, the oxide breakdown strength, or increasing the reverse bias junction [5 - 7]. It is therefore necessary to clean these surfaces to less than 10^{10} atoms/cm^2, using wet processes called RCA clean; established in 1970 [8]. An ultra-clean silicon wafer surface is (i) particle free, (ii) without organic contaminants, (iii) with minimized metallic contaminants, (iv) native oxide-free, (v) completely hydrogen-terminated, and (vi) with minimized surface micro-roughness. Diluted hydrofluoric acid solution (DHF), required to suppress native or chemical silicon oxide, is included in the cleaning sequence.

Should the HF solution be not perfectly pure, noble metal traces such as copper, silver, gold, or platinum could be deposited on silicon wafer surfaces during the first oxide removal step [9]. Nowadays, to prevent electrical breakdown, the miniaturization of MOS devices requires high purity chemicals, below the ppb or ppt level. The analysis of the metallic contamination of silicon surfaces after the cleaning step has become of great interest and can be quantified with a detection limit near 10^{10} atoms/cm^2 (reaching now 10^9 atoms/cm^2) using TXRF spectroscopy (Total Reflection X Ray Fluorescence) [10].

Torcheux et al. [11], and more recently Teerlinck et al. [12] have shown that the rate of elemental copper deposition is approximately proportionnal to the ion-concentration in solution, but decreases slightly with time, the effect being attributed to a diffusion rate determining step. The experiments by Chyan et al. [13] allow the determination of the kinetics of copper deposition from AFM microscopy evaluation. More recently, Parks [14] proposed an electrochemical approach of the process. This idea was elaborated by Chyan [15], who experimentaly demonstrated that electrochemical parameters could be very sensitive to trace amounts of noble metals present in DHF solutions.

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The copper adhesion mechanism is not clearly understood. More fundamental studies are required to establish a technology which prevents metallic contamination and to obtain characterization criteria for the surface state.

In the present work we have undertaken electrochemical and radioactivity measurements to study the mechanism of copper deposition on p and n-type silicon surfaces from DHF solutions containing traces of copper in the range of a few tens of ppb. In order to derive fundamental parameters describing the contamination mechanisms, we have limited the study to systems constituted by electronic grade silicon in contact with high purity deoxygenated DHF solutions, in the dark.

Assuming that copper contamination is an electrochemical process, we started an experimental study using a home built cell which allowed rest potentials and voltammetric curves to be measured with an excellent reproducibility. This new electrochemical cell, described in [16, 17], proved to be very sensitive for the detection of metallic impurities either contained in DHF solutions, or pre-existing on the silicon surfaces.

We propose hereafter a reaction scheme for silicon contamination by copper traces contained in DHF solutions. It will also be demonstrated that electrochemical techniques are extremely powerful to study silicon surface contamination by trace amounts of metallic ions.

Experimental

In our experiments, silicon wafers, 125 mm diameter and 625 μm thickness, were purchased from MEMC Electronic Materials:
p-type wafers, boron doped, ($5 \cdot 10^{16}$ at$\cdot$cm^{-3});
n-type wafers, phosphorus doped, ($2 \cdot 10^{14}$ at$\cdot$cm^{-3}).

These wafers were CZ grown and (100) oriented, one of the face was mirror polished, for CMOS applications, and the reverse side was mechanically polished as enhanced gettering to establish an ohmic contact, which facilitates the Ga-In deposition.

To obtain a reproducible surface state, the silicon samples were cleaned with a mixture of H_2SO_4:H_2O_2 (3:2) at 80°C during 10 minutes. In the semiconductor industry, this cleaning solution is the first treatment step which enables organic surface impurities to be oxidized, and a new silicon oxide layer to be grown. The sample is then thoroughly rinsed with deionized water and then cleaned by DHF solution to promote a pure oxide free silicon hydrophobic surface.

DHF solutions, 5% by volume, were obtained after mixing 40% HF SLSI grade (metallic elements concentration below 1 ppb) with pure deionized water. Before each experiment series, DHF was deoxygenated by bubbling argon gas N60 grade containing less than 0.1 ppm residual oxygen, during at least 2 hours. For the in-situ copper contamination experiments, we used a deoxygenated 5% DHF stock solution, containing copper ions, with a concentration of 2 ppm. An adjusted volume of this solution was transferred into the electrochemical cell containing 8 ml DHF deaerated solution.

The mechanism of copper nuclei formation on silicon plates immersed in DHF solutions, was investigated by two complementary techniques.

1. Electrochemical methods

These experiments were achieved with a home-built electrochemical cell, allowing for reproducible open-circuit potential recordings, by a rigorous control of the oxygen content, the exposition to light and the purity of the chemicals. The results are then extremely sensitive to several factors, such as the metallic electrolyte contamination and the existence of surface defects [15]. This cell was precisely described in [16, 17]. The silicon wafer was maintained in close contact with a Teflon tube, 2.5 cm diameter, filled with the electrolyte, this system being then pressed between two polyvinyl plates. The whole cell is protected against room light by means of a closed cylinder made of black polyvinyl polymer. The electrical contact on the reverse side of the silicon sample can be simply obtained with a gold foil, after dissolution of the native oxide; the contact resistance of the interface Au/Si was found to be less than 100 Ω. This value is negligible in the case of the determination of the potential at zero current, and for the measurement of the polarisation resistance, the current density being equal to a few nA. Only in voltammetric studies with current of several μA, the electrical contact was obtained after deposition of a Ga-In alloy layer. The counter-electrode was a small platinum plate, and the reference electrode was a saturated calomel electrode (SCE), connected to the electrolyte by means of a bridge made of a Teflon capillary tube filled with KCl jellied solution. The cell allowed for assays with an electrolyte volume of 8 ml, and a silicon samples of ~ 5 cm^2.

The electrochemical measurements were done with a Tacussel Radiometer Analytical PGS 201T potentiostat. This device was driven by an IBM PC computer using the Voltamaster software, allowing for the preselection of the experimental procedure. For example, in the case of open circuit potential measurements, the values were recorded at time intervals of one second. In the case of voltammetry, the scanning rate and lower and upper limits of the potential were preselected. Current response data were collected by the same microcomputer and stored in a memory file. Afterwards, data were transferred to a printer for drawing an *X-Y* graph and could be used for a mathematical treatment leading to the modellization of the processes.

Open circuit potential recording was quite useful because this parameter is a characteristic of the anodic and cathodic surface sites reactivity, the results being dependent on the electrolyte components and the surface states of the semiconducting electrode material. This parameter has recently gained high interest [18] because, for a long time, free potential was known to be not reproducible within a few hundred mV, as was already noticed by Föll [19]. Our electrochemical cell meets all the requirements for a quite reliable determination of the electrode rest potential.

Cyclic voltammetry has been extensively used during the last thirty years and has led to knowledge of silicon electrode reactions in various electrolytes. However, previous voltamperometric measurements often used a rather wide potential range lying in a few volts around the open-circuit potential, which seriously affected the silicon surface state, leading to the formation of porous silicon [20]. In the semiconductor industry, however, the silicon wafers are immersed in electrolyte solutions, so that they are only exposed to their own open-circuit potential. To be as close as possible to this situation, our voltamperometric measurements were recorded in a small potential range, mostly ± 50 mV around the rest potential for the determination of the polarization resistance leading to the corrosion current. In a few cases, the scanned range was ± 250 mV near the zero current value in order to obtain more precise information on anodic and cathodic electrode reactions.

2. *Radioactive ^{64}Cu indicator*

The contamination of silicon surfaces by metallic trace amounts is usually determined using TXRF spectroscopy. Our equipment, Rigaku 3726, allows for a quantitative and non destructive determination of the metallic elements deposited on a silicon surface. But this analytical technique is very sensitive to surface roughness, which scatters the fluorescence response and lowers the response signal detected by the Si-Li detector. TXRF is well adapted to smooth surfaces, but the roughness due to pitting corrosion, enhanced by metallic contamination, leads to inaccurate measurements [21].

Therefore, radioactivation analysis, which is not at all sensitive to surface roughness, has been undertaken in this study. Indeed, we wanted to settle a technique which could correlate each electrochemical potential measurement with the corresponding surface copper concentration of the same sample. This experimental method cannot be operated by TXRF analysis which needs an entire silicon wafer.

Experiments were undertaken according to two distinct paths: activation analysis and radioactive isotope indicators [22]. Neutron activation of elemental metallic copper leads mainly to ^{64}Cu, a β^-, β^+ and γ emitter with a half-life of 12,6 hours. The most specific method to detect the copper radiation is based on the use of either a Ge-Li semiconductor junction detector or a NaI-Tl scintillation well-type counter, using a narrow spectrum window around 511 keV, corresponding to the annihilation of the β^+ rays.

In the first method, the silicon surface was contaminated with DHF solutions containing trace amounts of copper ions, using the electrochemical cell previously described. These silicon samples were then exposed to a neutron flux (10^{14} neutrons/cm^2·s), in the Orphée nuclear reactor. The experiments were undertaken at the Pierre Süe laboratory, at the Saclay Nuclear Research Center (CENS). One disadvantage of this method is that the bulk impurities and silicon itself are also activated. But high resolution γ counting, using a Ge-Li detector, show up all the impurities of the sample, the integrated neutron flux being determined by a special gold monitor. For example, we have obtained the following values (Table 1) for the main impurities detectable in n-type silicon (doped

Table 1. Main impurities observed by neutron activation analysis, in Si wafer (only long lived isotopes are indicated).

Elements	Indicators	ng/g
Cu	^{64}Cu	3.3
Au	^{198}Au	0.051
Na	^{24}Na	51
K	^{42}K	84

$2 \cdot 10^{14}$ P atoms·cm^{-3}). Note that Na and K could be adsorbed species in the native silicon oxide layer.

From this result, it appears that 1 cm^2 of a wafer 600 μm thick, contains about $5 \cdot 10^{12}$ Cu atoms as bulk impurity. Then, only an excess surface contamination higher than $3 \cdot 10^{12}$ atoms/cm^2 can be detected by activation analysis.

In the second method we used ^{64}Cu as a radioactive tracer obtained by irradiation, in the same Orphée nuclear reactor, of a 0,5 mg high purity copper wire. This metal was dissolved in DHF so as to obtain a 1 ppm stock solution, which is subsequently diluted to obtain the different concentrations for each experiment. This method was more convenient because the radioactive emission was only due to ^{64} Cu. Moreover, it enabled to obtain both the electrochemical recordings and the quantitative Cu surface analysis, on the same silicon sample.

The protocol for the electrochemical parameter measurements was identical to that described hereupon, except that the copper contaminant was radioactive. As a control of the reliability of this procedure, we have ascertained that the potential versus time graphs were identical whether Cu was radioactive or not. Because of the short half-life of ^{64}Cu, all the experiments were undertaken on the same day as the radiotracer was received, 24 hours after the end of irradiation for annealing due to security regulations. The counting device, Autogamma Cobra II Packard Instruments, was programmed for repeating all the countings more than ten times, 10 min each, and included a software for data treatment introducing the radioactive decay correction. The blank background counting in the 511 keV energy window was found equal to less than 1 Bq, while a 10^{-2} μg Cu calibration sample indicated 68 Bq in the same conditions. The lower limit of detection by this method is estimated to be $2 \cdot 10^{11}$ atoms/cm^2, the area of the samples being approximately 5 cm^2.

Silicon samples were introduced in the electrochemical cell and then contaminated with a well known amount of radioactive copper in a deaerated solution of DHF in the dark. The open-circuit potential was recorded for a predetermined duration to control the reproducibility of the results. Then the cell was immediately emptied, the sample was thoroughly rinsed with deionized water and transferred to the automatic counting device. This method, which enabled electrochemical recordings and radiochemical analysis on the same silicon sample, was very useful to establish a correlation between the electrochemical response and the surface density of Cu nuclei.

Results

The metallic copper deposition was known for a long time as resulting from an electrochemical reaction of copper ions in DHF solution with silicon surface atoms. In the earliest experiments [9], copper concentrations were very high ($\sim 10^{-2}$ mol/l), whereas the actual concentrations in cleaning solutions lie in the few ppt to few ppb range. In the previous models describing the electrochemical reaction, the contamination mechanism was supposed to involve electrons contained in the solid semiconductor electrode.

$$Cu^{2+} + 2e^-_{Si} \rightarrow Cu_{metal},\ E^\circ = +\,0.340\ \text{V/SHE}. \quad (1)$$

In order to clarify the deposition mechanism, and more particularly the role played by majority and minority carriers, a few workers [23] have undertaken contamination experiments to compare the behavior of p and n type silicon. If copper reduction proceeds via electron tunnelling transfer, n-type silicon should be more reactive for copper reduction. However, the most recent results of Parks [14], obtained with TXRF measurements, seem to indicate that copper was reduced at the same rate, whether the silicon wafer is p- or n-type doped. Moreover in a fundamental study of the silicon/DHF interface electrochemical properties [18], it appeared that charge transfer reactions on cathodic sites result from the electrons generated by the corrosion process of the silicon substrate in DHF electrolytes.

$$Si + 2\,F^- \rightarrow SiF_2 + 2\,e^-,\ E^\circ = -1{,}2\ \text{V/SHE}. \quad (2)$$

Naturally, this simple reaction is followed by successive electrochemical and chemical steps leading to $[SiF_6]^{2-}$ ions in solution, according to the mechanism proposed by Rieger and Kohl [24].

Electrochemical measurements are quite interesting because the silicon/electrolyte interface can be characterized in situ, by recording the open-circuit potential versus time. This study proved that copper reduction, at the level of a few ppb, could be detected as soon as copper ions are introduced in the DHF electrolyte, and that open-circuit potentials values are characteristic of cathodic and anodic surface sites reactivity. Moreover, in order to interpret the behavior of minority and majority carriers, we have undertaken

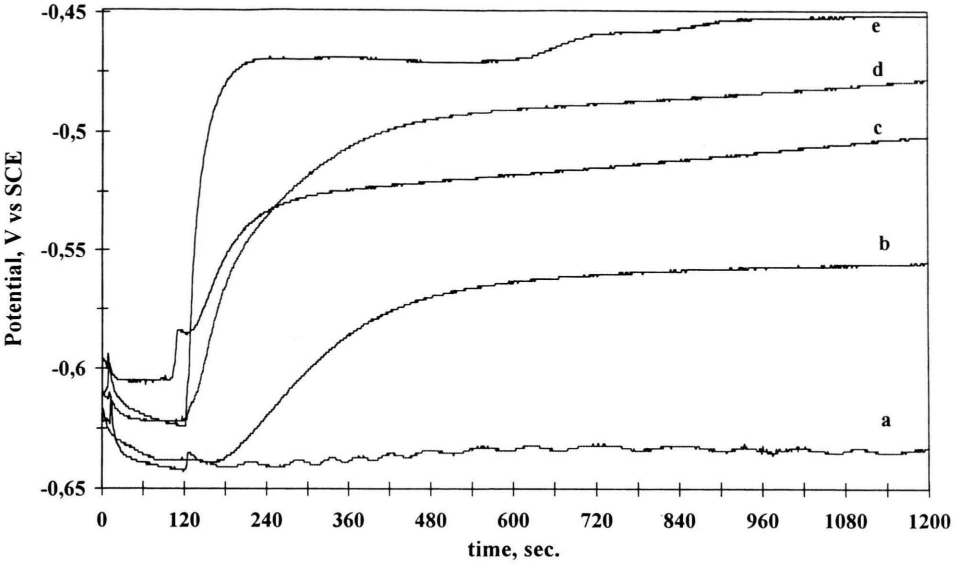

Fig. 1. a) Time dependence of the open circuit potential of p-type silicon, in the dark, in contact with a perfectly deoxygenated 5% DHF solution, upon addition of trace amounts of copper: O ppb (a), 15 ppb (b), 39 ppb (c), 74 ppb (d), 260 ppb (e).

voltamperometric records within a narrow range of potential around the open-circuit potential.

Copper reduction kinetics was obtained, using rest potential measurements at regular intervals of 1 second during approximately 20 minutes. At first, for each sample, the rest potential curve was recorded on p and n type silicon substrates immersed in pure deaerated DHF, in the dark, during an initial period of 2 minutes. The observed open-circuit potential, –650 mV, was consistent with our previous results [18], indicating that the DHF solution was really pure, and Si substrate really clean. We can also notice that the five experimental results obtained for each substrate almost coincide. This excellent coincidence, allows for the detection of any potential perturbation resulting from a change of reactivity of the surface sites. Then, a small volume, 1 ml, of deaerated DHF solution containing copper ions (Cu^{2+}) was added, so that the copper concentration, in the electrochemical cell, reached 15 to 1200 ppb.

The addition of trace amounts of copper contaminant was observed to result in a sudden shift of the potential towards positive values, as shown in Figs. 1(a) and 1(b). Immediately upon copper ion addition the rest potential increased at a rate nearly proportional to the copper concentration, and then tended rapidly to a stable limiting value. The reference experimental curve, resulting from the addition of pure deoxygenated DHF under the same conditions, was nearly flat. So, we think that rest potential is characteristic of the silicon surface reactivity modified by the reduction of copper ions, whether the silicon substrates were p or n-type doped. According to the usual models for mixed potentials, this variation should be ascribed to a steep increase of the ratio i_c / i_a corresponding to cathodic and anodic site exchange current.

To explain more precisely the shape of these rest potential curves, we have recorded, on each silicon sample, the voltamperometric characteristics, presented in Figure 2. When the current intensity is zero, the curve gives the open-circuit potential which is identical to the final values indicated in Figs. 1(a) and 1(b). This experiment reveals the anodic and cathodic electrode behavior, showing very clearly that the cathodic current is amplified while the anodic current remains nearly unchanged.

From this result, the question arises whether the increase of the cathodic current should be assigned to the reduction of Cu^{2+} ions. In order to separate the contribution of proton reduction on cathodic sites, we have contaminated silicon samples in our electrochemical cell with deaerated DHF containing 15, 40, 75, 260 ppb of copper ions. These contaminated surfaces were then thoroughly rinsed with pure deionized

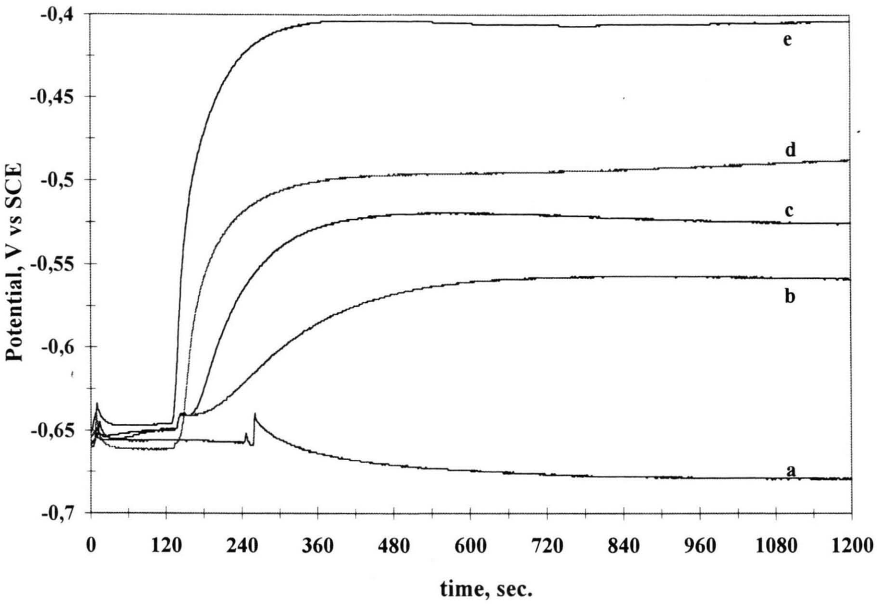

Fig. 1. b) Same as Fig. 1a, but for n-type silicon.

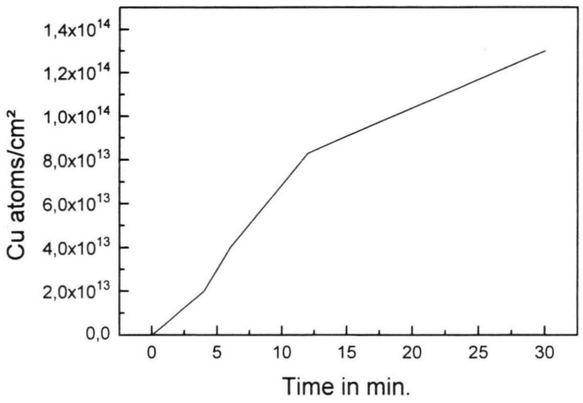

Fig. 2. Voltamperometric curves of the n-type silicon samples used in Figure 1b, after copper contamination in DHF solutions: 0 ppb (a), 15 ppb (b), 39 ppb (c), 74 ppb (d), 260 ppb (e).

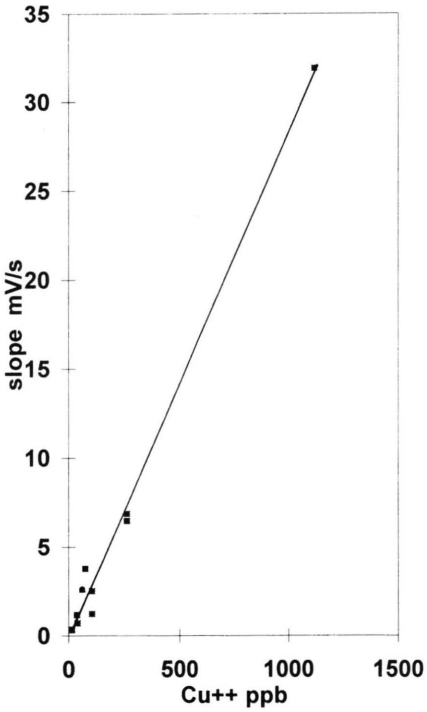

Fig. 3. Graph showing the relationship between the ascending part of the O. C. P. slope and copper concentration in DHF solutions.

water, to keep the surface free from electrolyte traces. Then, again, voltamperometric curves were recorded with these samples contacting a perfectly pure deaerated DHF solution. These curves were found to be identical as those obtained in the presence of trace amounts of copper impurities (Fig. 2), showing that cathodic current increases with surface copper concentration. The result suggests that the cathodic current in DHF is mainly related to the discharge of protons on copper nuclei which act as catalyst.

We also notice that the slope of the ascending part of the open-circuit potential curve should be approximately a linear function of the copper ion concentration like the generation rate of metallic clusters. This slope has been measured on p and n-type silicon

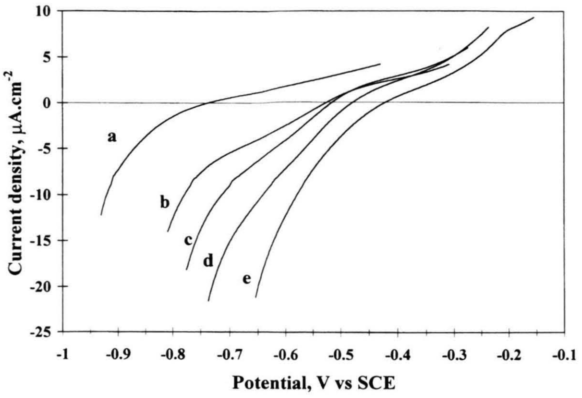

Fig. 4. a) Copper contamination kinetics, using radioactivity, on an n-type silicon sample, maintained in the dark, in completely deoxygenated DHF, containing 100 ppb Cu^{2+}.

and reported on Figure 3. The linear relationship was verified, and it seems that there is no significant difference between the behavior of p- and n-type silicon.

As the cathodic current is nearly proportional to the copper nuclei area, what is the significance of the potential plateau exhibited on all curves of Fig. 1(a) and (b)? Does it mean that the metal deposition ends after a short time following the ascending part of the graph? To clarify the silicon contamination by copper ions and the shapes of the rest potential graphs, more quantitative information about the copper reduction is required. Radioactivity analysis was very efficient in this research program. Firstly, we mentioned that radioactive copper behaves like natural copper with respect to silicon surface, the electrochemical response being identical in both cases. Figure 4(a) shows the density of copper atoms reduced on an n-type silicon surface, as a function of the immersion time in DHF, as determined with radioactive copper tracer. This investigation results in a kinetic approach to copper reduction on silicon substrates. We notice that the copper deposit grows continuously, even after a few tens of minutes, suggesting that the open-circuit potentials are not directly related to the surface copper concentration, because the electrochemical (Fig. 4(b)) and radiochemical curves, do not show the same shape. Voltamperometric experiments lead to the conclusion that the open-circuit potential curves are characteristic of cathodic and anodic reactions on silicon surfaces. The comparison of quantitative radiotracer data of the surface density of metallic contaminants with potentiometric response of the same samples (Fig. 5) indicated that the first generated nuclei subsequently grow without any substantial enhancement of their catalytic properties.

The growth of copper clusters must involve electrons from electrochemical etching of the silicon

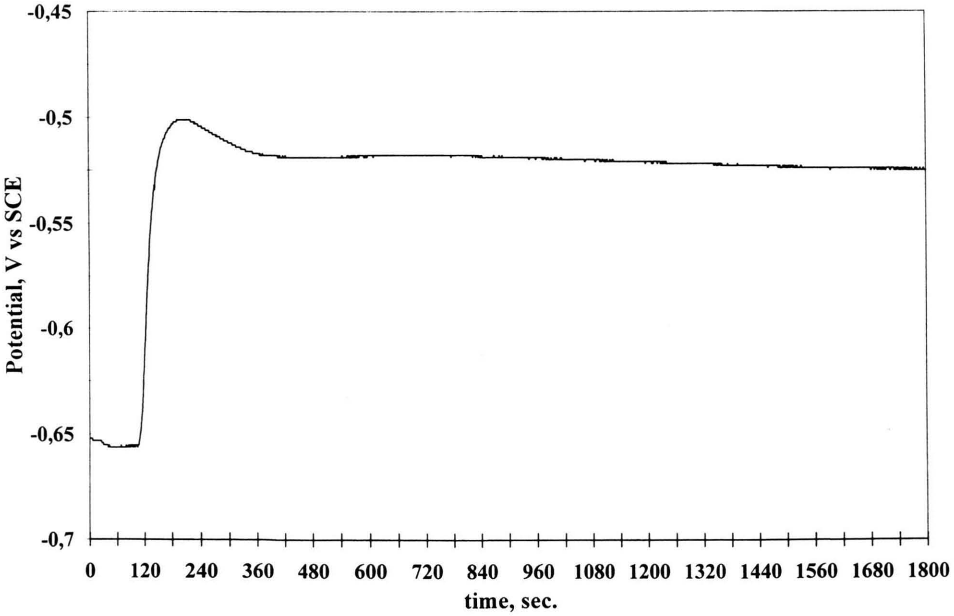

Fig. 4. b) Copper contamination kinetics. O. C. P. as a function of time. Same experimental conditions as Figure 4a.

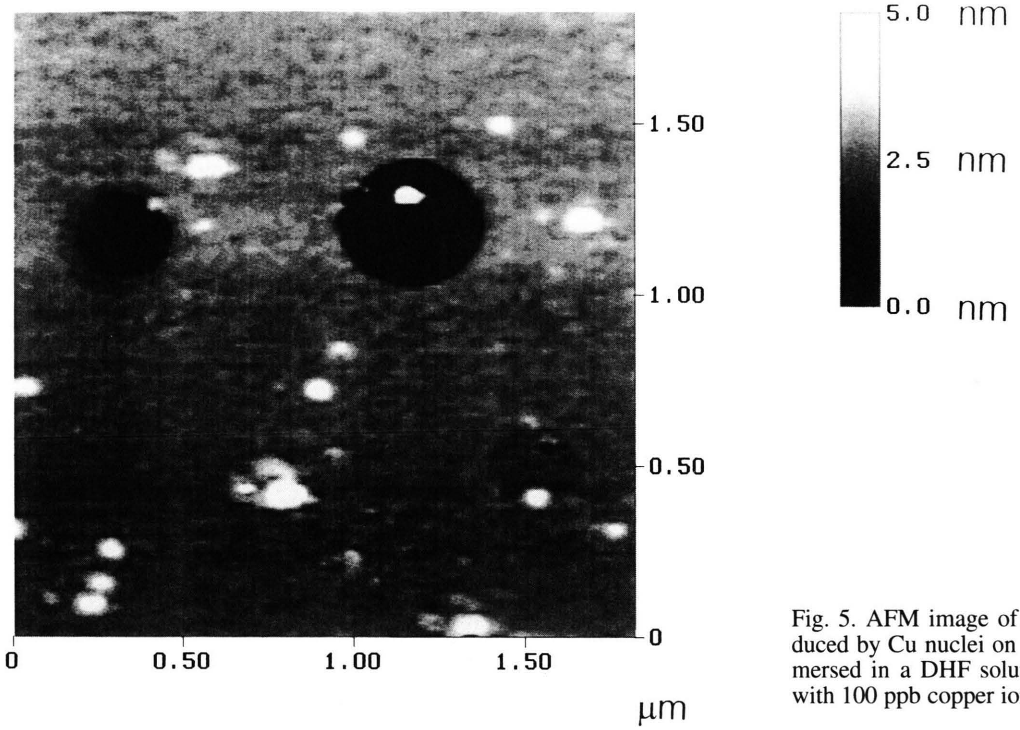

Fig. 5. AFM image of corrosion pits induced by Cu nuclei on n-type silicon immersed in a DHF solution contaminated with 100 ppb copper ions.

substrate. Depending on the density of the nuclei, dissolution process could be distributed over the whole silicon surface. However, owing to the current lines which tend to follow the minimal ohmic resistance in the solution and in the semiconducting material, the reaction should induce initiation of corrosion pits. Therefore we have completed the preceding experiments by studying the morphology of a silicon surface contaminated by copper ions with an atomic force microscope (Digital Instruments, Nanoscope III), working in tapping mode. Figure 6 shows the surface structure of an n-type silicon sample, contaminated with copper, in a deaerated DHF solution, in the dark. Copper atoms form small nuclei, sometimes situated at the center of a corrosion pit, as the result of the catalytic properties of cathodic copper sites. The first copper nuclei generate the dissolution of a very small amount of Si substrate. But, subsequently, they constitute a local electrochemical cell and induce an intense proton discharge current which in turn results in a deep pitting of the silicon wafer.

Discussion

Electrochemical measurements proved to be very sensitive for the dectection of metallic ultra-traces. A potential perturbation in DHF solutions containing metallic impurities was observed by Parks et al. [14], although their electrochemical measurements seem to be not well defined because physical parameters, such as dissolved oxygen and photon flux, were not controlled. Parks has postulated that almost all of the copper deposition occured in the first few seconds, although, in a previous publication [25], the results indicated a continuously increasing copper deposition during 25 min. from a buffered etchant solution. This last observation is in agreement with our radiochemical measurements, where copper ions are continuously deposited on the silicon surface during 30 minutes, but the rate gradually decreases (Fig. 4) as result of a diffusion process through a depleted region around the initial crystals [11]. We conclude that, the response of the O.C.P. is not closely related to the density of copper atoms on the silicon surface.

Now, the shape of the potential/time curves (Fig. 1(a), 1(b)) obtained upon addition of copper contaminant in the DHF solution show a plateau for which interpretation requires a closer analysis. The existence of this plateau has very recently been confirmed by Chyan et al. [15]. A tentative explanation could arise from their previous observations [13] of silicon surface by atomic force microscopy. Their experimental results demonstrated that the number of copper grains increases rapidly during the first minute and then reaches a constant value. It follows that the continuous increase of the copper deposit, observed by our radiochemical measurements, results from the growth of all nuclei without change of their number.

In a previous publication [26] we recalled that the O. C. P. depends on the relative intensity of the anodic and cathodic current. In all cases, only one reaction can occur on the anodic sites. It corresponds to elemental silicon dissolution following reaction (2), which generates electrons in the semiconductor. On the other hand, these electrons are consumed on cathodic sites following three distinct paths:

$$\begin{array}{lll} Cu^{++} & + 2e^- & \rightarrow Cu_{Si} \\ H^+ & + e^-_{Si} & \rightarrow H_{Si} \\ H^+ & + e^-_{Cu} & \rightarrow H_{Cu} \end{array} \qquad (3)$$

From the computation of the radiotracer measurements, the contribution of the Cu^{++} discharge to the overall cathodic current appeared to be negligible. On the other hand, the discharge of protons can be divided into two components, one corresponding to the sites on the silicon substrate the other to those on the copper nuclei. The O. C. P. equation for E_r suggests a discussion about the ascending part of the rest potential curves. This equation is

$$E_r = \frac{\alpha E_1^0 + \beta E_2^0}{\alpha + \beta} + \frac{RT}{nF(\alpha + \beta)} \ln \frac{j_{0C}}{j_{0A}}, \qquad (4)$$

where j_{0C} and j_{0A} are the exchange current densities, characteristic of the rate with which the electronic interface transfers proceedes on cathodic and anodic sites.

This equation reveals that the direct measurement of the open-circuit potential gives information about the relative reactivity of the anodic and cathodic sites. Copper nuclei occupy only a small fraction of the silicon surface ($\theta \approx 1\%$). The total exchange current of protons (j_{0H}) can be expressed as a function of the silicon and the copper areas, respectively:

$$j_{0H} = (1 - \theta) j_{0H/Si} + \theta j_{0H/Cu}. \qquad (5)$$

The hydrogen evolution reaction (H. E. R.) exchange current on a high purity flat silicon surface $j_{0H/Si}$ has been estimated to lie between 10^{-10} and 10^{-11} A cm^{-2} [26] owing to the passivating properties of the Si-H bonds, whereas the exchange current for the same H. E. R. on metallic copper nuclei $j_{0H/Cu}$ was known to be approximately 10^{-7} A cm^{-2} [27].

To evaluate the overall j_{0H} on cathodic sites, we have simulated the curves presented in Fig. 2 with the Butler-Volmer equation [28]. Thus, electrochemical parameters, related to the exchange current on anodic and cathodic sites are obtained and lead to a comparison of the results as a function of copper concentration. The current is a function of the anodic (j_{01}) and cathodic (j_{02}) exchange currents, α and β represent the transfer coefficients and j_{sat} is the saturation current related to minority carrier diffusion [27]:

$$j = \frac{j_{01} \exp\left(\frac{\alpha(E-E_1)}{\phi}\right) - j_{02} \exp\left(\frac{\beta(E-E_1)}{\phi}\right)}{1 + \frac{j_{01}}{j_{sat}} \exp\left(\frac{\alpha(E-E_1)}{\phi}\right)}. \qquad (6)$$

The parameters were adjusted using an IBM microcomputer so that the experimental and calculated curves coincide with a good approximation. This procedure enables exchange currents of protons to be quantified. These values, and all electrochemical parameters such as j_{0Si}, j_{0H}, α and β, i. e. the transfer coefficients for Si oxidation and H reduction respectively, are listed on Table 2, as functions of the copper concentration in DHF solution. The influence of j_{sat} was negligible.

Table 2. Electrochemical parameters for anodic and cathodic site currents as determined by simulation of (6).

$[Cu^{2+}]$, ppb	α	j_{0Si} en A/cm^2	β	j_{0H} en A/cm^2
0	0.12	8.10^{-8}	0.35	$5 \cdot 10^{-9}$
15	0.15	$2 \cdot 10^{-8}$	0.25	$2 \cdot 10^{-7}$
37	0.20	$5 \cdot 10^{-9}$	0.17	$4 \cdot 10^{-7}$
74	0.20	$5 \cdot 10^{-9}$	0.20	$8 \cdot 10^{-7}$
260	0.20	$5 \cdot 10^{-9}$	0.26	$1 \cdot 10^{-6}$

An important result appearing on this table is that cathodic currents on pure silicon surface are a hundred times lower than those corresponding to the contaminated silicon by trace amounts of copper. Also, we notice that the cathodic exchange current grows with copper addition. However, probably as a result of some uncertainty in the model adjustment, the relation between copper concentration and cathodic exchange current is not strictly linear. These results led us to the conclusion that copper nuclei act as cathodic sites which promote proton reduction. Moreover, the anodic exchange current is almost constant and is not modified by traces of copper contamination.

From these results we suggest a tentative model for the metallic contamination of Si surfaces. Following the general concepts for crystallization phenomena, the metal deposition should proceed in two successive steps: i) generation of nuclei and then ii) growth of the crystals.

Starting from the expression of the mixed potential (4), we write

$$E_r(t) - E_r(0) = \frac{RT}{nF(\alpha + \beta)} \ln \frac{j_{0C}(t)}{j_{0A}(0)}, \tag{7}$$

where $E_r(0)$ and $E_r(t)$ are the rest potentials of a pure and contaminated silicon surface at the time t during the copper deposition. Similarly, $j_{0C}(0)$ and $j_{0C}(t)$ are the corresponding cathodic exchange currents which are extracted from the modeling procedure. The total cathodic current at t time, being a function of the cathodic exchange current of protons on silicon surface $j_{0H/Si}$ and on copper nuclei $j_{0H/Cu}$, respectively:

$$j_{0C}(t) \cong j_{0H/Si} + \theta(t) \cdot j_{0H/Cu}. \tag{8}$$

Then,

$$\frac{j_{0C}(t)}{j_{0C}(0)} = 1 + \frac{\theta(t) j_{0H/Cu}}{j_{0H/Si}} \tag{9}$$

and

$$E_r(t) - E_r(0) = \frac{RT}{nF(\alpha + \beta)} \frac{\theta(t) j_{0H/Cu}}{j_{0H/Si}}. \tag{10}$$

During the first step, as $\theta(t)$ is a linear function of the density of copper clusters, we assume that the generation rate of nuclei should be approximately proportional to the concentration of copper ions in solution. Then, during the rather short time corresponding to the ascending part of the potential vs time graph we can write

$$\frac{\delta E_r(t)}{\delta t} = \frac{RT}{nF(\alpha + \beta)} \frac{j_{0H/Cu}}{j_{0H/Si}} \frac{\delta \theta(t)}{\delta t} \cong kC_{Cu^{2+}}. \tag{11}$$

Figure 3 gives a confirmation that the slope of the ascending part of the potential/time variation is approximately proportional to the copper concentration in solution. Moreover, we should underline that Fig. 3 shows that the same regression line seems to be available for both n- and p- type silicon samples. This observation supports Parks results [25], and suggests that the properties of the silicon/electrolyte interface depend more on the electrochemical surface reactions than on the semiconductor electronic carriers properties.

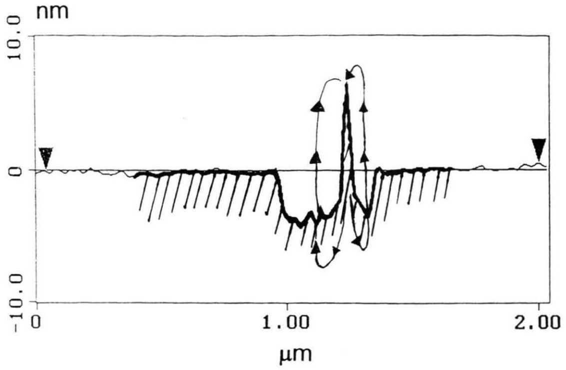

Fig. 6. Section profile around a copper nucleus, from Figure 5.

During the second step, we assume that the number of nuclei remains constant and that their size grows with time. Under these conditions, the external area of the metal grains should increase following a $t^{2/3}$ relation, which would result in a slowing down of the potential variation. However, in order to give an interpretation of the appearance of the potential plateau, despite the continuous increase of deposited copper, we suggest that the catalytic properties of metallic clusters for protons discharge decrease as the crystals size grows. This well known property of catalytic materials [29] would explain the very rapid potential variation during the initial period of small nuclei generation, and the appearance of a limiting constant value when the crystals growth result in the formation of large size particles with poor catalytic activity.

Finally, the high catalytic activity of metallic nuclei must induce a rapid local corrosion of the substrate as a consequence of the formation of a short-circuited electrochemical cell. For this reason, we observed contaminated silicon surfaces using AFM microscopy working in the tapping mode. We recall that, in a first oversimplified assumption, the dissolution of Si substrate, which is necessary to supply the electrons, should be directly correlated to the copper reduction. Under this hypothesis, only a very little amount of silicon atoms should be involved. In fact, the high level of current density due to the protons reduction is responsible for a rapid dissolution of the substrate. In most cases the short-circuit current has to follow the minimal ohmic resistance lines, in the solution as well as in the semiconductor. The current lines are focussed on the cathodic site whereas a corrosion pit is initiated nearby. Figure 6 shows a striking illustration of this mechanism. In this figure, current lines were drawn on the section profile from AFM analysis, the depth of the initiated pit being approximately 3.5 nm. Naturally, we have also observed that pits get much deeper when the sample is maintained for a long time even though the DHF solution should be of high purity.

Conclusion

Experimental investigations using a new electrochemical cell, described previously, completed with radioactive tracers analysis, have permitted successfully to describe the silicon behavior in contaminated DHF solutions.

In this study we have mainly developped the fundamental aspects leading to the mechanism of silicon surface contamination by metallic traces. For this reason, all experiments have been undertaken with thoroughly deaerated DHF solutions, in the dark.

The mixed potential was considered as representing the relative activity of both cathodic and anodic sites distributed on the silicon surface.The results led to the conclusion that, after a first step where the first copper nuclei are formed, the catalytic properties of these particles promote a high cathodic current density due to protons discharge. This catalytic effect was very efficient at the early stage of copper nuclei formation. During the growth of copper grains, their catalytic properties decreased, which could explain the limiting value of the rest potential. This interpretation was provided by radioactive measurements which revealed that contamination proceeded continuously with a nearly constant copper deposition rate during at least 30 minutes (in our experiments).

One of the main results of this work is that our electrochemical cell revealed to be very sensitive to the presence of metallic traces as well in DHF solution as on silicon surfaces. Although the response signal is not specific for the contaminant identification, it could be a powerfull tool, in the semiconductor industry, for on-line monitoring of the cleaning solutions during chemical processing.

The strong proton reduction currents, on copper grains, generates an intense corrosion current, leading to the local initiation of pits on anodic sites. Our interpretations are in good agreement with classical electrochemical concepts applied to semiconductors.

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