

2000-08-28

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Recommended Citation

Xuan CHENG, Chang jian LIN. Electrochemical Investigations of Semiconductor Silicon Wafers[J]. *Journal of Electrochemistry*, 2000 , 6(3): 258-264.

DOI: 10.61558/2993-074X.1387

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol6/iss3/2>

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Electrochemical Investigations of Semiconductor Silicon Wafers

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Abstract : Electrochemical characteristics of semiconductor silicon wafers were investigated in dilute hydrofluoric acid solutions using DC polarization and AC impedance techniques under both illuminated and dark conditions. Both techniques were extremely sensitive to the trace amount (10^{-9} wt % level) of copper presented in solutions , but only sensitive to the 10^{-6} wt % level of non-ionic surfactant OHS contained in solutions. The results revealed that the electrochemical reactions took place favorably and became predominated at silicon/ solution interface under illuminated condition.

Key words : Polarization Resistance ,Copper contamination ,Silicon/ solution interface

CLC number : O 645.54 **Document code :** A

1 Introduction

The group IV element-silicon plays an important role in the development of solid state electronics. Microelectronics and silicon chips have almost become the synonymy due to the wide applications of silicon materials in semiconductor device manufacturing.

Silicon etching in hydrofluoric acid system is one of the fundamental steps in microelectronic processing since aqueous fluoride solutions have been commonly used in chemical etching , lithography and wet cleaning^[1]. Metallic contamination on silicon wafer surfaces during wet cleaning processes represents the main cause for poor performance and poor reliability of electronic devices^[2~4]. Copper deposition onto silicon surfaces from liquids has been most widely recognized due to its fast diffusion rate and deleterious effect on device yields^[5~7]. It is , therefore , important to identify and to detect trace amounts of copper in solutions , accordingly , to control metallic

Received Date : 20 Jan. 2000

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Foundation item : Supported in part by Scientific Research Foundation for Returned Overseas Chinese Scholars from the State Ministry of Education of China.

contamination in device manufacturing.

In this work, the electrochemical characteristics of semiconductor silicon wafers in dilute hydrofluoric acid solutions were investigated by performing DC polarization and AC impedance measurements at room temperature under illuminated and dark conditions. Different concentrations of copper and of non-ionic surfactant OHS were intentionally added into solutions to examine the nature of copper contamination and the effect of surfactant on silicon surfaces.

2 Experimental

2.1 Samples and Chemicals

Both p(100) (1 ~ 10 μcm) and n(100) (2 ~ 4 μcm) single crystal silicon wafers were provided by Texas Instruments. All the chemicals used [H_2SO_4 (98 %), H_2O_2 (30 %), HF (49 %), and non-ionic surfactant OHS (20 %)] were of semiconductor grade and provided by Olin Company. ICP copper standard solutions (1000 10^{-6}wt %) were purchased from Sigma Chemicals.

2.2 Electrochemical Measurements

The electrochemical DC polarization measurements, started from open-circuit potentials towards either anodic or cathodic direction at a scan rate of 0.5 mV/s, were carried out using an EG&G Model 273 A Potentiostat/ Galvanostat and PC computer and software. The AC impedance measurements were performed using an EG&G Model 6310 frequency analyzer response combined with Model 273A Potentiostat/ Galvanostat and PC computer, and the related software package. The exciting signal used was ± 5 mV sine wave with frequencies ranging from $10^5 \sim 10^{-2}$ Hz. The 3-electrode cell was modified from an EG&G Model K0235 Flat Cell by using polypropylene as the cell body with a volume about 170 ml. The working electrode was silicon wafer (1.5 \times 1.5 cm^2), the exposed area to solutions was fixed to 1 cm^2 . The auxiliary electrode was Pt flake, and the reference electrode was Ag/AgCl double-junction electrode. Before each measurement the wafer was cleaned in 4:1 by volume H_2SO_4 : H_2O_2 mixture solutions for 10 minutes, then rinsed by deionized water (18 M $\Omega\text{-cm}$), followed by dipping the wafer into 2 % HF solutions for 30 seconds and rinsed by deionized water, finally dried by carefully spraying nitrogen gas to the wafer surface. The illumination was provided by 100 W tungsten, and the dark condition was under the black box with all lights in the laboratory being turned off. All the tests were carried out at room temperature (25 \pm 1 $^\circ\text{C}$).

3 Experimental Results

Typical polarization and impedance curves obtained with p-type and n-type silicon in dilute HF solutions under both illuminated and dark conditions are shown in Figs. 1 and 2, respectively. It is apparent that both techniques are extremely sensitive to the trace amount (100 10^{-9} wt %) of copper presented in solutions.

As depicted in Fig. 1, the illumination remarkably influenced the open-circuit potentials

(E_{ocp}) of p-type and n-type silicon. No matter whether copper was present in solutions, the values of E_{ocp} for p-type became more cathodic, while those of n-type more anodic. When no copper was added into solutions (Fig. 1(I)), the illumination had minimal influence on polarization resistance (R_p) which is an inverse measure of electrochemical reaction rate and can be obtained from the intersection by extrapolating the linear portion of both anodic and cathodic parts at small overpotentials. However, the positions of E_{ocp} for each curve were apparently changed. Conversely, the presence of $100 \cdot 10^{-9}$ wt % copper in solutions significantly increased the reaction rate under illuminated condition, as indicated by the increase in R_p values, i. e., the curves had been shifted to the right direction where the current densities became larger (Fig. 1(II)).

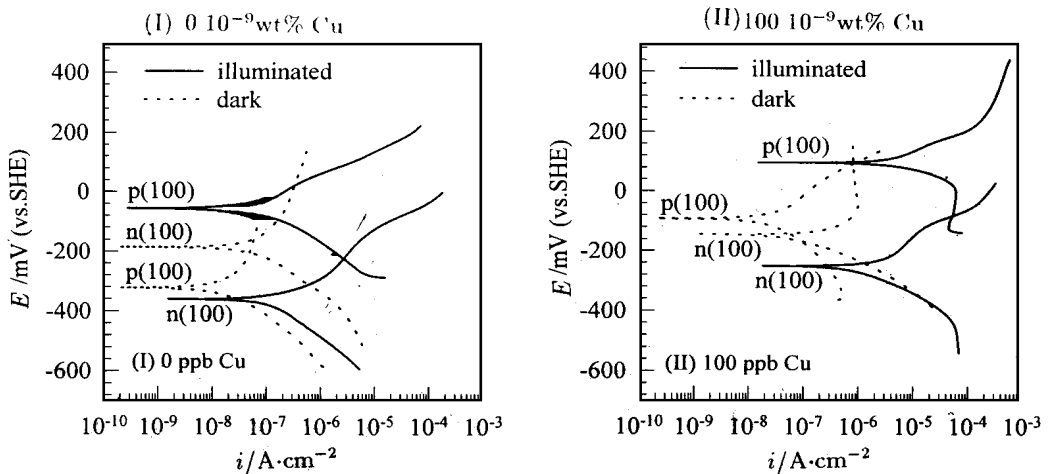


Fig. 1 Typical polarization curves obtained with p(100) and n(100) silicon wafer electrodes in the absence and presence of $100 \cdot 10^{-9}$ wt % copper under illuminated and dark condition.

In Fig. 2, the experimental data obtained by AC impedance measurements were best fitted by theoretical simulation lines with the R_p values being indicated on each curve. More detailed analysis on the impedance measurements can be found elsewhere^[7]. Under illuminated condition, typical semi-circular behavior was observed in copper-free solutions, therefore the reaction was under activation control (Fig. 2(a) & Fig. 2(b)); when $100 \cdot 10^{-9}$ wt % copper was added into solutions, the semi-circles were shrunk, suggesting the decrease in R_p values, and additional inductive loops were observed. The appearance of inductive behavior was characteristic of copper deposition onto silicon surfaces from solutions^[7]. However, the R_p values became very large under dark condition (Fig. 2(c) & Fig. 2(d)), implying the electrochemical reactions occurred at the silicon/solution interface is not practically feasible under the dark. In fact, both p-type and n-type are in depletion region and their semiconductor properties become predominant under dark condi-

tion^[7].

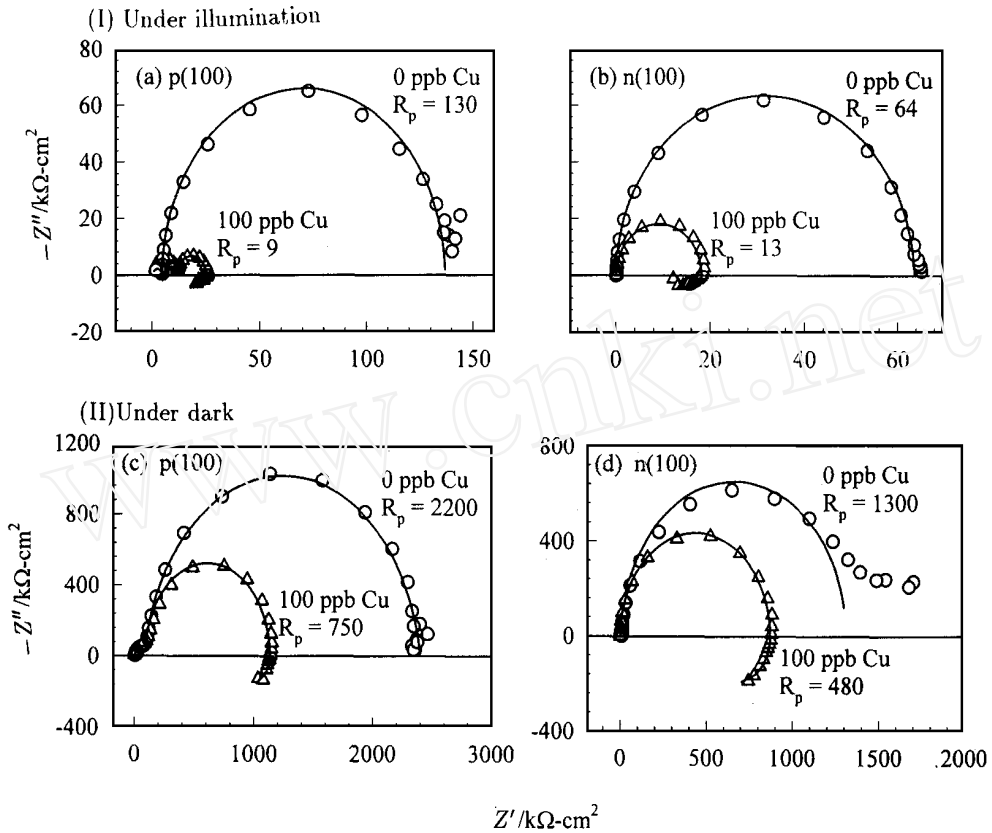


Fig. 2 AC impedance spectra obtained with p(100) and n(100) silicon wafer electrodes in copper-free and 100 10^{-9} wt % copper-contaminated HF solutions. (a) (b) under illumination; (c) (d) under dark.

To examine whether the electrochemical techniques are sensitive to the presence of surfactant in solutions, the polarization curves of n-type silicon under illuminated condition when different concentrations of non-ionic surfactant OHS were added into dilute HF solutions are provided in Fig. 3. The impedance plots obtained with p-type silicon in the presence of various OHS concentrations under the illumination are shown in Fig. 4. It is noticed that the electrochemical behaviors of both n-type (Fig. 3) and p-type (Fig. 4) silicon significantly varied when the 10^{-6} wt % level of OHS was added into solutions under the illumination. The increase in R_p values with the increase of OHS concentrations suggests that the electrochemical reactions occurred at silicon/solution interface when OHS was adsorbed on silicon wafer surface become slower. However, the impedance responses were not so sensitive to the 10^{-9} wt % level of OHS presented in solutions, as evident in Fig. 4. The polarization measurements made by p-type silicon in the presence of

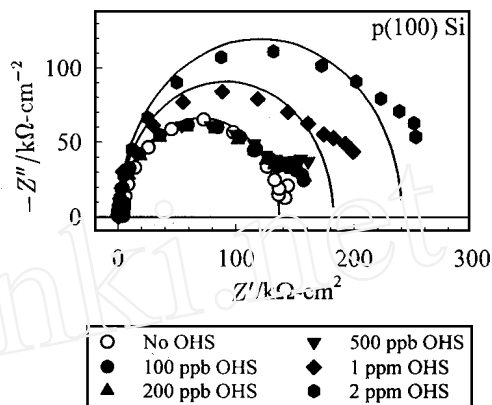
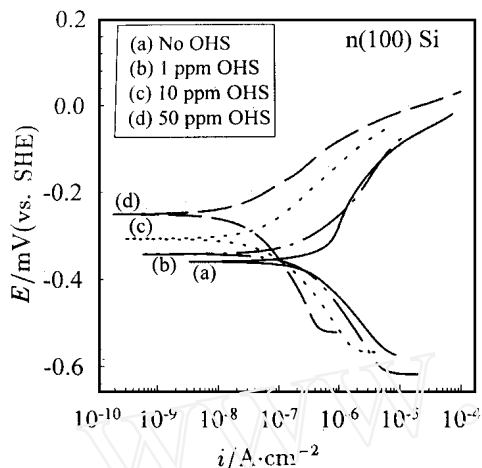


Fig. 3 Typical polarization curves obtained with n (100) silicon wafer electrodes in the absence and presence of various concentrations of OHS surfactant under illuminated condition.

Fig. 4 Typical impedance plots for p (100) silicon wafers in the absence and presence of various concentrations of OHS surfactant under illuminated condition.

10^{-9} wt %-level of OHS under illumination (data are not shown here) confirmed with this observation.

4 Discussion

In general, the electrochemical reaction occurred at the silicon surface in dilute HF solutions can be represented as



The oxidation of silicon takes place at the anodic area of silicon/ solution interface and produces electrons or consumes holes. The hydrogen ions in solutions can be simultaneously reduced at the cathodic area of silicon/ solution interface.



If there are copper ions present in solutions, the oxidation of silicon will be accelerated because the potential of copper deposition is higher than that of hydrogen reduction.



It is therefore expected the decrease in R_p and increase in E_{ocp} when copper is present in solutions. The experimental results shown in Figs. 1 and 2 agreed well with the above analysis. As given in Fig. 1(I), the cathodic behavior of both p-type and n-type silicon shows a typical Tafel linear response, indicating that the reaction is under activation control. When 100×10^{-9} wt % copper was added into the solutions (Fig. 1(II)), the linear response was only valid at low overpo-

tentials, a transition occurred at higher overpotentials, implying that the reaction mechanism has been changed. Since the transport of copper ions from the solution to the vicinity of electrode surface became an important factor at higher overpotentials, the reaction is under concentration control, hence, a limited current density was observed. The AC impedance results given in Fig. 2 are also consistent with the DC polarization results, as evident by the decrease in R_p values and the appearance of characteristic inductive loop in the presence of 100×10^{-9} wt % copper.

Fig. 5 compares the polarization resistance (R_p) of p-type silicon measured by both DC polarization and AC impedance techniques under illuminated conditions as a function of copper concentration ($[Cu^{2+}]$) presented in solutions. As can be seen from Fig. 5, the values of R_p significantly decreased as the increase of copper concentration in solutions, indicating the acceleration of electrochemical reactions at the silicon/solution interface. It is interesting to note that an excellent linear relationship (in a Logarithmic-Logarithmic plot) existed between the polarization resistance measured by the electrochemical techniques and copper concentration presented in solutions. This suggests that the electrochemical techniques can be potentially applied to fast detection in the 10^{-9} wt %-level of copper contamination during wet processing of silicon wafers.

As shown in Fig. 5, the values of R_p measured by DC polarization and AC impedance were approximately the same in copper-free solutions, however, they differed from each other in the presence of copper contamination, in particular, deviated as the increase of copper concentration in solutions. The values of R_p measured by DC polarization were larger than those measured by AC impedance in copper-contaminated HF solutions. The main factors contributed to this difference include: (1) the polarization technique requires applying larger bias potentials (typically ± 250 mV), this may cause a damage on silicon wafer surfaces, while the impedance technique only applies small exciting potentials (usually ± 5 mV); and (2) the values of R_p measured by DC polarization were obtained by carefully extrapolating the linear portions of both anodic and cathodic curves at small overpotentials, through which the significant errors may be introduced when the typical linear relationship is not held. The R_p values can, however, be directly calculated by AC impedance technique. Hence, the R_p values obtained by AC impedance technique are more accurate than those obtained by DC polarization technique.

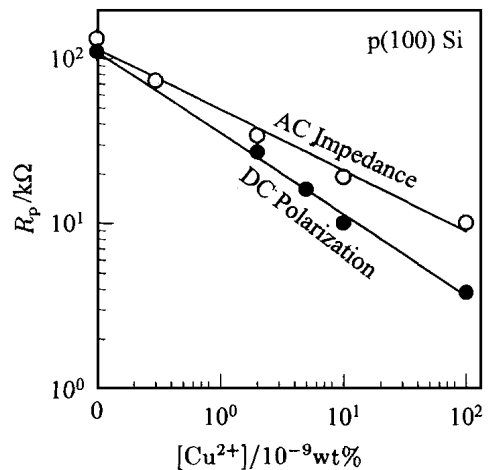


Fig. 5 A comparison on polarization resistance as a function of copper concentrations in HF solution measured by DC polarization and AC impedance techniques.

5 Conclusion

The electrochemical characteristics of semiconductor silicon wafers were investigated in dilute HF solutions by DC polarization and AC impedance techniques. Under illuminated condition, electrochemical reactions took place favorably at silicon/ solution interface, while the semiconductor properties became predominate under dark condition as indicated by the extremely large values of polarization resistance. It was found that the electrochemical techniques are very sensitive to the 10^{-9} wt %-level of copper presented in HF solutions and both techniques can be potentially applied to wet cleaning processes for sub-micron technology to detect and to control copper contamination.

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半导体硅片的电化学研究

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摘要: 采用电化学直流极化和交流阻抗技术,在有光照和黑暗条件下分别研究了半导体硅片在稀释氢氟酸溶液中的电化学特性.两种电化学技术均对溶液中含有的微量铜(10^{-9} wt %-浓度水平)非常敏感,但仅对溶液中的 10^{-6} wt %-浓度水平的非离子型表面活性剂敏感.结果表明,有光照条件下在硅/溶液界面上极易发生电化学反应,且该反应对硅表面性质起主导作用.

关键词: 极化电阻,铜沉积,硅片/溶液界面