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CHEMICAL ETCHING OF MONO AND POLY-CRYSTALLINE SILICON IN $HF/K_2Cr_2O_7/H_2O$ SOLUTIONS *

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In this work an experimental study on the etching reaction of low-doped silicon was carried out in $HF/K_2Cr_2O_7/H_2O$ mixed solutions. The morphology of the etched surface was examined with varying HF and $K_2Cr_2O_7$ concentration, reaction time and agitation speed. The surface of etched wafers were analysed using SEM (scanning electron microscope) and EDX (Energy-dispersive X-ray). The structure of porous silicon films created by etching in $HF/K_2Cr_2O_7$ is shown to depend on the solution composition and the resistivity of the silicon substrate. The investigation of the $HF/K_2Cr_2O_7$ system on polycrystalline silicon surface shows that in the concentration range $1 \div 2$ M of potassium dichromate ($K_2Cr_2O_7$), the surface is microporous. The texture developed is a network of hemispherical tubs. It is seen that reflection losses in micropores (tubs) decreased greatly, to be comparable with the defect etchants method and much lower that obtained by Stocks et al. Simultaneous porous silicon growth and deposition of hexafluorosilicates has been observed. Taking into account this observation a dissolution mechanism of the silicon is proposed.

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1 Introduction

The interest in porous silicon (PS) has increased greatly over the last decade, mainly due to its photoluminescence (PL) and the potential applications, which arise from these. There are however, many other uses including micromachining, chemical sensors, mirror filters, etc. Porous silicon is usually prepared by anodization of silicon in aqueous hydrogen fluoride (HF). However, for highly resistive crystalline and amorphous silicon an instability, which limits the maximum thickness of the nanoporous layer can be observed [1].This instability was explained by the large resistivity value of the silicon (PS) in comparison with that of the electrolyte [2]. In order to increase the maximum thickness of PS several strategies may be considered: (i) varying the resistivity of the electrolyte (ii) illumination of the sample (injection of carriers), (ii) (photo) chemical etching. Instead of conventional porous silicon anodization by electrical bias applied to an electrochemical cell, an appropriate mixture of HF, $K_2Cr_2O_7$ and H_2O has been studied under various reaction conditions. $HF/K_2Cr_2O_7/H_2O$ solution has long been used as one of HF-oxidizing agent-H_2O solutions, and reported as a good etching solution because of no formation of stains on the silicon surface after etching [3–5]. In order to elucidate the pore morphology

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and the etching mechanism, the etch rates were examined with varying HF and $K_2Cr_2O_7$ concentrations, reaction time and agitation speed. Finally, the etching solution has been applied for texturing polycrystalline silicon .It is known that wet chemical is a potential method of texture polycrystalline silicon wafers.

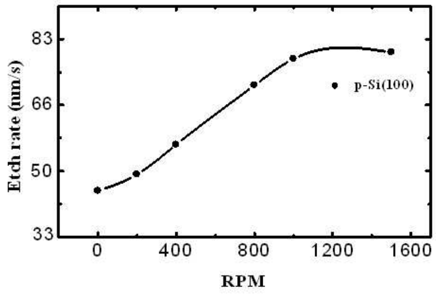
2 Experimental

P-type Si(100) single crystal wafers manufactured by Wacker with Czochralski technique were used in this experiment. The p-Si was boron doped and had a resistivity in the range of 0.01 Ωm to 20 Ωm. Polycrystalline silicon material used in this work was from Baysix (from Bayer AG) with a resistivity of 0.01 Ωm. The substrate were chemically polished on one side in $HF/HNO_3/CH_3COOH$ (1/4/3 by vol.) solution, during 120 s . Silicon specimens of 10 x 10 mm^2 was etched in a cylindrical polyethylene reactor chemical of electronic grade and deionised water were used to prepare an etching solution of 50 ml. The experimental data were taken in the etching solution of various compositions. The etching solution was stirred sufficiently enough to exclude the effect of mass transfer on the liquid-solid reaction. The etch rate was obtained with dividing the etched amount of Si by reaction time, exposed surface area and Si density. The surfaces of etched wafers were analysed using SEM (scanning electron microscope), FTIR (Fourier transform infrared spectroscopy and EDX (energy-dispersive X-ray).

3 Results

The effect of agitation speed of the etching solution on etch rate of silicon was examined in the etching solutions of $HF/K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) with the variation of the agitation speed from 0 to 1500 RPM. The result is shown in Fig.1. It is seen that the etch rates of Si increases with the agitation speed up to 800 RPM and then reaches a satured value. The linear variation observed in the etch rate at low speeds is attributed mainly to ineffective mass transfer of the reaction species near the silicon surface [6]. However, the mass-transfer rate of the species through the liquid-solid interface is greatly increased at higher agitation speeds, favoring silicon etching. Therefore, to neglect the effect of mass transfer, all experiments are performed at 800-1000 RPM. It is interesting to notice that independly of component concentration and agitation speed of the solution, the stains are not observed at the etched surface.

The effect of the etching time on the rate was examined by measuring the etch depth as a function of etching time (300, 600 and 1800 s). The etch depth was calculated by dividing the etched amount of silicon, i.e., a weight difference of Si before and after the etching process, by surface area exposed to the etching solution and silicon density (2.33 x 10^3 kg/m^3). The etch depth was also compared with that measured by scanning electron microscopy (SEM). The etch rate was determined by dividing the etch depth by the reaction time. The formation of an insoluble white layer on the silicon surface was noticed. Surface imaging, realized via scanning electron microscopy, shows the presence over the Si surface of a homogeneously distributed crystal assembly thick (Fig.2). The thickness of the deposited layer on Si Surface depends on the $K_2Cr_2O_7$ concentration. It should be noted that the presence of crystal assembly is found more important in the $< 111 >$ oriented Si surface. The crystal concentration increases in the order $< 100 >< < 110 >< < 111 >$. Elemental analysis by EDX revealed that the films are mainly



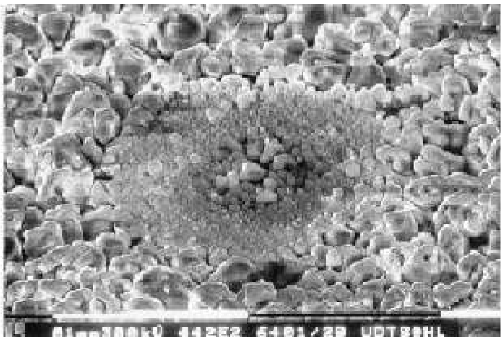
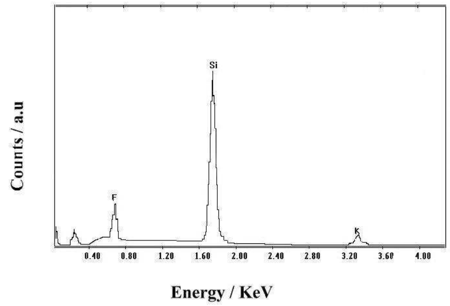


Fig. 1. The effect of agitation speed on etch rate in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.

Fig. 2. Scanning electron micrograph of the passivating layer formation HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.



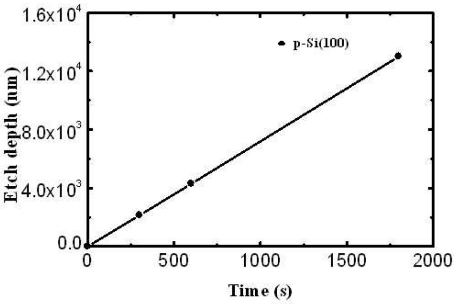


Fig. 3. Energy dispersing layer formed in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.The spectrum is consistent with the composition K_2SiF_6.

Fig. 4. The effect of reaction time on etch depth in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.Speed 800 RPM.

composed of Si, F and K**,** Fig.3.Hexafluorosilicate K_2SiF_6 has always been considered as the final reaction product in the dissolution mechanisms.

Fig.4 corresponds to the etching of silicon in HF/$K_2Cr_2O_7$(1.5 M) (2/1 by vol.) solution at 293 K and 800 RPM. It shows that the etch depth increased linearly with time, indicating that the etch rate of silicon is constant during the etching reaction.

The effect of $K_2Cr_2O_7$ concentration on the etch rate was examined in HF/ $K_2Cr_2O_7$ (2/1 by vol.) solution with the variation of $K_2Cr_2O_7$ concentration from 0.15 to 2.5 M for constant HF concentration (24 M). The results are presented in Fig.5. It is seen as the $K_2Cr_2O_7$ concentration increases, the etch rate increases to reach a maximum value at about 1.15 M and then decreases.

The morphology of the porous Si layer was examined by SEM. The plane and cross sectional views provide information on the geometry of the horizontal and vertical cross sections of the pores, respectively. The shape of the pores is found to be dependant on the $K_2Cr_2O_7$

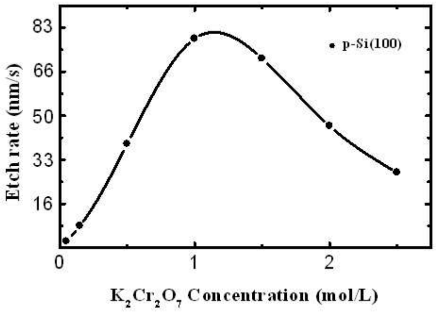


Fig. 5. The effect of $K_2Cr_2O_7$ concentration on the etch rate in HF/$K_2Cr_2O_7$ (1.5 M)(2/1 by vol.) solution. Speed 800 RPM

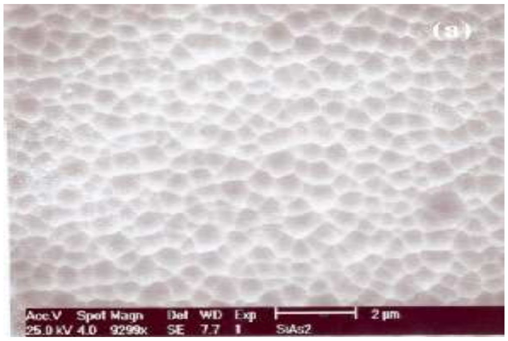


Fig. 6. SEM photographs of p-Silicon. a) $\rho = 0.1\Omega m$ b) $\rho = 1\Omega m$

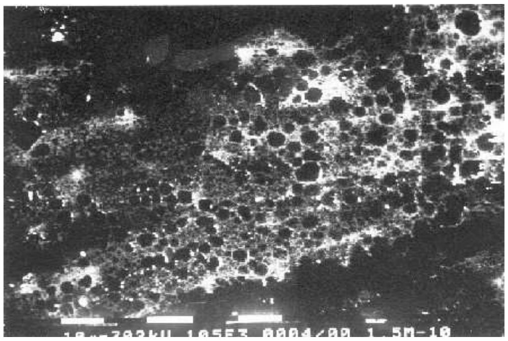


Fig. 7. The effect of changing oxidant $K_2Cr_2O_7$ concentration on the pore diameter in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.

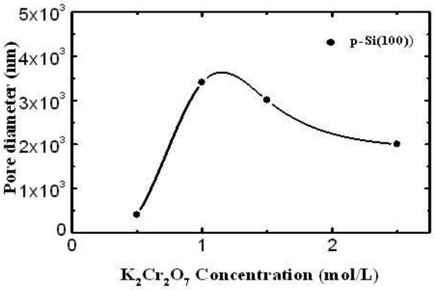


Fig. 8. The variation of pore diameter as function silicon resistivity in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution.

concentration. The pore sizes depends on the oxidant concentration, the amount of charge transferred and doping density. For 0.1 Ωm resistivity samples, a honeycomb lattice of hexagonal pores are observed, while for above and higher than 1 Ωm, macropores with rounded shape were observed, Figs. 6.(a) and (b), respectively. Interestingly, the structures observed on Fig.6a are highly regular.It is seen that as the $K_2Cr_2O_7$ concentration increases, the average diameter of the pores increases to reach a maximum value at about 1 M and then decreases. Fig.7 shows the effect of changing oxidant concentration on pore diameter, $K_2Cr_2O_7$ concentration was varied over a range from 0.5 to 2.5M. As soon as the solution is put into contact with the silicon, a visible gas evolution occurs. The observed hydrogen evolution is much greater from the high-doped, compared to the low doped material. This effect is consistent with the basic Si etching mechanism [7–9] which is initiated by the reaction of holes with Si atoms at the etching surface.

The surface morphologies of PS on substrates with various silicon resistivity (ρ_s) values formed after HF/$K_2Cr_2O_7$ etching shows that porosity level increases with increasing ρ_s. As a consequence, the pore diameter increases with decreasing ρ_s. For HF/$K_2Cr_2O_7$ (1.5 M)(2/1 by vol.) concentration solution, it Varies from 0.3 x 10^{-3} mm for 0.01 Ωm to 4 x 10^{-3} mm for 21.1 Ωm, Fig.8. Wehrspohn reported a mean diameter value of the pores in highly resistive or amorphous silicon about 3 to 5 x 10^{-3} mm [10].

The effect of HF concentration was studied with varying HF concentration 5.8 M to 19.33M for fixed $K_2Cr_2O_7$ concentration of 1.5 M. The measured etch rates are shown in Fig.9. It is seen that the etch rates increases very slowly at HF concentration lower that 14 M, but increases rapidly for concentration higher than 15 M. This evolution is similar to that reported, with low $K_2Cr_2O_7$ concentration, by several authors [11, 12]. The results were explained by the fact that the rates maintain low values at lower HF concentration because the amount of HF required for dissolving $SiO_2$is deficient and consequently the undissolved SiO_2 layer prevents further reaction. When a small amount of HF was added to the solution an increase in the rate of the oxide formation was observed. In the same way, it was found that F^- (or HF) accelerate the oxide formation as well as the dissolution rate of the oxide, resulting in the acceleration of the etch rate at high HF concentration [9]. In addition, the holes on the valence band drift toward silicon surface due to the energy difference between the valence band of Si and the redox potential of etchant, resulting in the increase of hole concentration on the silicon surface. The increased hole concentration not only accelerates the etch rate but also the formation of K_2SiF_6 layer. The etching mechanism of HF/$K_2Cr_2O_7$ based systems has been well studied in the case of crystalline silicon [7, 12, 13]. The formation of the porous layer can be understood as a local electrochemical process in which the reaction is chemically initiated. Microscopically, anode and cathode sites are formed on the etched surface resulting in a local current flux. The chemical process has to incorporate a source of excess holes and electrons for the charge transfer between the electrode. In the case of $K_2Cr_2O_7$, used as an oxidizing agent in making an etching solution, $Cr_2O_7^{2-}$ ion react with H^+ to form holes (h^+) on the silicon surface according to the following reaction [14].

$$Cr_2O_7^{2-} + 14H \rightarrow 2Cr^{3+} + 7H_2O + 6h^+ \tag{1}$$

For p-type Si, it is generally accepted that the reaction proceeds entirely via the valence band and can be expressed in the following way

$$Si + 2HF + 2h^+ \rightarrow SiF_2 + 2h^+ \tag{2}$$

To account for the hydrogen formation, the divalent silicon is transformed into Si (IV) by the following possible reaction [8]

$$SiF_2 + 4HF \rightarrow H_2SiF_6 + H_2(g) \tag{3}$$

or

$$SiF_2 + 2H_2O \rightarrow SiO_2 + 2HF + H_2(g) \tag{4}$$

followed by

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{5}$$

The dissolution reaction may then proceeds schematically as

$$Si + 6HF + \lambda h^+ \to H_2SiF_6 + 4H^+ + (4 - \lambda)e^- \tag{6}$$

The oxide is formed by a reaction which involves the participation of four holes

$$Si + 2H_2O + 4h^+ \to SiO_2 + 4H^+ \tag{7}$$

$$SiO_2 + 6HF \to H_2SiF_6 + 2H_2O \tag{8}$$

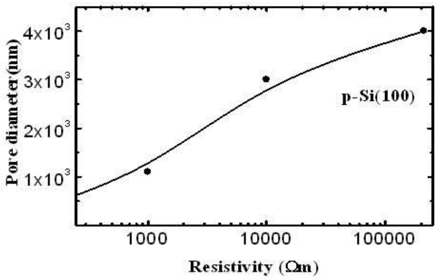
In addition, Gerisher et al [15] have suggested that SiF_6^{-2} was formed on the silicon surface during the silicon dissolution and the limiting process might be the mass transport of the product species from the surface into the bulk solution.
Resulting finally in soluble SiF_4 or SiF_6^{-2}.

$$SiF_2 + 2HF \to SiF_2 + H_2 \tag{9}$$

$$SiF_4 + 2F^- \to SiF_6^{-2} \tag{10}$$

4 Application to polycrystalline silicon - Reflectance measurements

The investigation of the HF/$K_2Cr_2O_7$ system on polycrystalline silicon surface shows that for $K_2Cr_2O_7$ concentration below 1 M, the etch is preferential. However, at low etching time (t<180 s) and for $K_2Cr_2O_7$ concentration up to 1 M, the etching becomes anisotropic, similar to that generally obtained with KOH or NaOH solutions. The morphology of the surface varied with etching time and becomes porous, Figs.10a and 10b. The pore diameter increases with time. SEM observation of polycrystalline Si surface etched in $K_2Cr_2O_7$(1.5 M)/HF (1/2 by vol.) during 300 s. is shown in Fig.10a. The magnification of the Fig.10a shows that the surface is formed by a network of tubs (Fig.10b). The pore diameter reaches 1 x 10^{-3} mm value for 600 s. etching time. The etch rate is constant. The surface observed in Fig.10a appeared uniform on all silicon surface. Similar results were reported by stocks et al [16] , which reported a formation of hemispherical tubs with an isotropic etch consisting of 50% HF / 70% HNO_3/ 85% H_3PO_4 in the ratio 1/5/30. Tubs shows considerably less reflection than an anisotropically (KOH) etched sample. Reflection losses in tubs decreased greatly, An early application of porous Si in photovoltaic was reported 20 years ago [17]. The work was addressed to the minimization of the optical losses in mono and polycrystalline Si based solar cells. A lowering of the reflectance from 37% to 8% was measured with respect to the bare substrate (monocrystalline). However, when porous silicon (PS) is formed on polycrystalline Si, the integrated reflectance in the 300-900 nm spectral region is around 10% [18].Reflectance measurements of variety samples were made using Cary 500 spectrophotometer with an attached integrating sphere. Polycrystalline samples were 300 μm thick. Fig. 11. summarises the best results of the total reflectance, R, as a function of wavelength for silicon wafers etched using various etching conditions. Are plotted also their bare as-cut and polished substrates for comparison. It is seen that reflection losses in micropores (tubs) decreased greatly (less than 13.5%), value lower than that of defect etchants method and much lower than that obtained by Stocks et al. (25%) [16]. The reflection losses for a bare as-cut



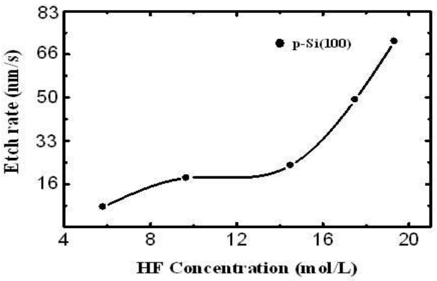


Fig. 9. The effect of HF concentration on the etch rate of silicon in HF/$K_2Cr_2O_7$ (1.5 M) solution with varying concentration.

Fig. 10. Measured reflectivity of polycrystalline silicon surface. polished as-cut etched in HF/$K_2Cr_2O_7$ (1 M) (2/1 by vol.) solution. Etching time 180 s.

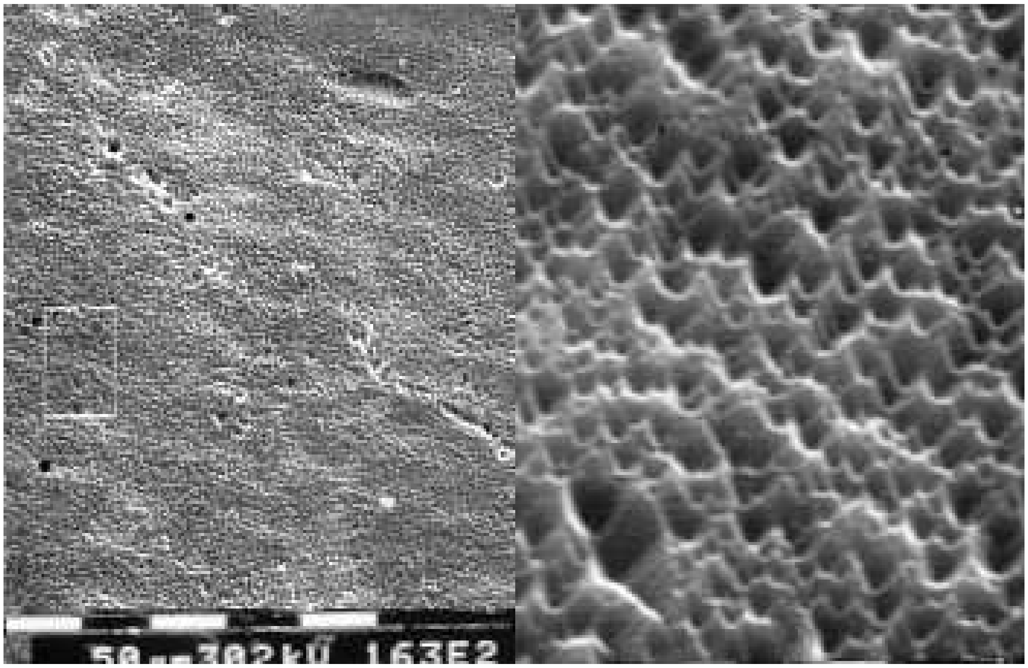


Fig. 11. a) SEM photograph of polycrystalline silicon after 300 s in HF/$K_2Cr_2O_7$ (1.5 M) (2/1 by vol.) solution. b) 8 x magnification.

polycrystalline silicon is about 26%, much lower that a polished one (37%).The results obtained on polycrystalline silicon can be improved by changing the experimental conditions (concentration, time, temperature…). With a defect etchants based on the HF/HNO_3/CH_3COOH system a reflectance of 15% has been obtained on cast Silso silicon, depending on the etching conditions and the defect density of the material. However, the problem with this later technique is the reproducibility of the results [19].

5 Conclusion

The chemical etching of silicon in HF/$K_2Cr_2O_7$ (0.5 - 2.5 M) (1/1-2 by vol.) solution has been investigated under various reaction conditions. It was observed that the etch rate increased with the etching solution up to 800 RPM a then reaches a saturated value. It was shown that as the $K_2Cr_2O_7$ concentration increases the etch rate increases to reach a maximum value at about 1.25 M and then decreased, probably due to the formation of K_2SiF_6 observed on silicon surface depending on oxidant concentration and crystal orientation .The average diameter of the pores follows the same variation as the etch rate. In addition, reflectance measurements made with a variety of etching conditions on polycrystalline silicon show a lowering of the reflectance from 38% to 13.5% measured with respect to the bare polished substrate.

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