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CHEMICAL ETCHING OF ISOLATION GROOVES IN HIGH-POWER SILICON DEVICES

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The procedure of wet chemical etching, which plays an important role in the fabrication of high-power Si devices in standard commercial equipment, is discussed. The characteristics of isolation grooves in Si high-voltage thyristors and diodes have been investigated, with respect to etchants and wet etching conditions. It has been found that the standard deviation in the depth values of isolation grooves produced in the Si wafer of 125 mm in diameter is reduced to 0.85 μm using a proposed modified technological procedure.

Keywords: wet chemical etching, silicon high-power devices

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1. Introduction

Etching in acid or alkali solutions is one of the basic procedures in the fabrication of high-power Si devices. Silicon dissolves in fluoric acid and alkali solutions, whereas insoluble oxide film is formed on Si surface in reactions with other etching reagents. In the case of etchant composed of HF and HNO_3, the solution of Si proceeds in several stages, each of which is followed by changes in chemical composition of both Si wafer and etchant [1]. The etching rate and surface morphology of Si are dependent on the concentration of acids and reaction product H_2SiF_6. Silicon acid H_2SiF_6 formed in the reaction is considered to be a strong acid comparable to sulfurous acid [2]. H_2SiF_6 is formed in a two-step process. In the first step, Si is oxidized by HNO_3 resulting in formation of SiO_2. In the second step, Si oxide SiO_2 reacts with HF, forming SiF_4 that gives rise to SiF_6^{2-} by reacting with excess HF. The total reaction is [2]

$$3\mathrm{Si} + 4\mathrm{HNO_3} + 18\mathrm{HF} \to 3\mathrm{H_2SiF_6} + 4\mathrm{NO} + 8\mathrm{H_2O}\,. \tag{1}$$

Recent investigations have shown [3] that the etching mechanism of silicon is more complicated than that described by (1). Firstly, the oxidation of Si is caused by equilibrium reaction between nitric acid and nitrogen oxide [4]:

$$2\mathrm{HNO_3} + 3Ra \to 3Ra\mathrm{O} + 2\mathrm{NO} + \mathrm{H_2O}\,, \tag{2}$$

where Ra is a reducing agent. Secondly, nitrogen monoxide generates nitrous acid that is a dominant oxidizing reagent:

$$\mathrm{H^+NO_3^-} + 2\mathrm{NO} + \mathrm{H_2O} \to 3\mathrm{HNO_2}\,, \tag{3}$$

$$2\mathrm{HNO_2} + Ra \to Ra\mathrm{O} + 2\mathrm{NO} + \mathrm{H_2O}\,. \tag{4}$$

In the absence of HNO_2, the Si etching rate is very low [4] as the etching proceeds only due to reaction of Si with primary nitric acid. Therefore, in order to control the etching process, the reducing reagent should be used.

It is known that hydrogen and carbon are effective reducing elements. In etchants, acetic acid CH_3COOH can be used as reducing reagent, which determines formation of NO and HNO_2 and dilutes the concentrated acids. CH_3COOH is a better solvent than water because of its permittivity (6.15) which is lower than that (81) of water. As a result, a lower dissociation and a higher oxidation degree of HNO_3 are achieved during the etching process. In addition, a lower polarity of acetic acid, as compared to water, leads to a better wetting of a partially hydrophobic Si surface [5].

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It should be noted that the formation of deep isolation grooves in Si wafer with p–n junctions by wet etching differs from the etching process of a homogeneous substrate. During the etching process, hydrogen atoms penetrate into Si lattice, hence passivating p-type impurities like boron and resulting in a formation of a higher resistivity layer [6]. This process modifies the etching rate and the surface morphology of grooves, influencing simultaneously the breakdown voltage of high-power Si devices. Therefore, in order to improve the electrical parameters of Si devices, the chemical composition of etching solutions is to be carefully selected and the optimal etching conditions should be determined.

In conventional machining, the etching process and resulting quality of Si devices are also dependent on the stiffness of equipment and mechanical disturbances like vibrations and thermal deformations of the workpiece and machine [7]. Therefore, conventional machining properties should be optimized along with the control of wet etching process.

In this work the formation process of isolation grooves by wet etching procedure was analysed. The dependence of structural parameters of isolation grooves on the mechanism of etching procedure has been investigated in the fabrication process of thyristors and high-power Si diodes produced in "Vilniaus Ventos Puslaidininkiai". The chemical composition of acid etchants was optimized and the etching process was modified in order to improve the characteristics of fabricated devices. As a criterion of the effectiveness of the modified procedure, standard deviation of the depth of isolation grooves in Si wafers was considered.

2. Investigated structures

As substrates, n-type Si wafers of resistivity 60–120 Ω cm, diameter 125 mm, thickness 0.37 mm, and (111) crystallographic orientation were used. The p–n junctions in the diode and thyristor structures have been formed by diffusion of boron and phosphorus for producing the p- and n-type regions, respectively. The resulting carrier concentrations in p- and n-type regions were $2{\cdot}10^{18}$–$1{\cdot}10^{14}$ and $6{\cdot}10^{13}$ cm^{-3}, respectively. The arrays in wafers were separated by isolation grooves formed by wet chemical etching technique. Commonly, the grooves of 100 μm in depth and 800 μm in width were etched using $HF:HNO_3:CH_3COOH$ [(3–1.7) : (2–4) : (0.7–2) (v/v)] mixtures. In a further technological process, the grooves were filled with SiO_2-PbO-Al_2O_3-B_2O_3 compound which was melted into the glass by heating at 750–760 °C.

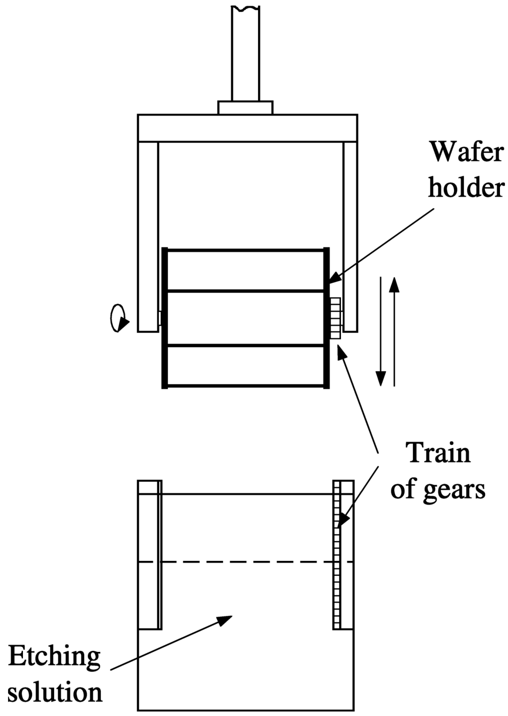


Fig. 1. A sketch of apparatus for etching the isolation grooves.

3. Experiment

In the fabrication of high-power Si devices, the industrial apparatus installed in "Vilniaus Ventos Puslaidininkiai" was used. The sketch of wet-etching equipment is presented in Fig. 1. The etching cell with 25 wafers was immersed in etching solution. The cell was moving up and down and rotated along the horizontal axis by means of the train of gears. The temperature during the etching process was controlled.

The depth of the grooves was measured making use of a contact stylus of DekTak 6M profilometer (Veeco). The numerical results presented in this work are based on the experimental data obtained in 655 runs of the measurements of isolation grooves in 131 Si wafers. The depth d of isolation grooves was measured at 5 points in each wafer. The average depth $\bar{d}$, depth range $R = d_{\text{max}} - d_{\text{min}}$, where d_{max} and d_{min} are maximum and minimum values of depth, respectively, and standard deviation $s_d = \sqrt{[\Sigma(d_i - \bar{d})^2]/(i-1)}$ $(i = 5)$ were calculated for each Si wafer.

4. Results and discussion

In order to improve the characteristics of fabricated high-power Si devices, the main attention was paid to the etching process. In processing of high-power Si devices, the quality of etching is characterized by the range R of the depth values and the profile of isolation

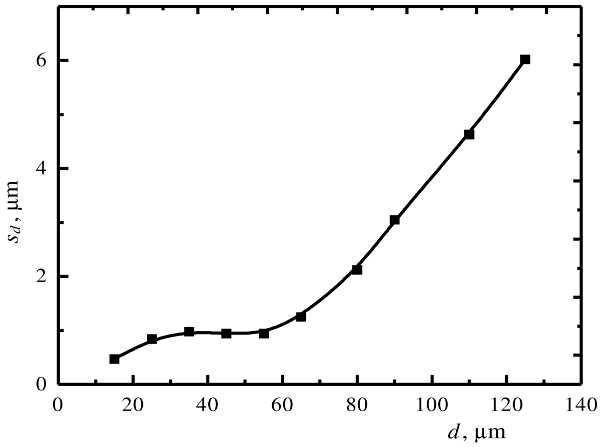


Fig. 2. Dependence of values of the standard deviation in depth on the depth of isolation grooves formed by wet-etching technique. Etching cell rotated at a speed of 38 rpm. The curve is a guide to an eye.

grooves in wafer. The R values determine mechanical characteristics of wafer, such as hardness, which are important in further technological procedure.

Experimental data showed that R values as well as standard deviation s_d (Fig. 2) increased with increasing d values. The s_d values presented in Fig. 2 were determined for isolation grooves formed on Si wafers etched at a standard speed of 38 rpm. As seen from Fig. 2, the depth-dependence of s_d is a non-monotonous function with a particular point at $d \sim 70$ μm corresponding to the location of the p–n junction. The s_d values are almost independent on depth in the p-type region whereas a steep increase is noticed in the n-type region. This observation is in agreement with the etching rate for p- and n-type Si [6]. A low etching rate in p-type Si has led to low values of R and s_d, whereas in the n-type region at larger d values a higher etching rate caused an increase of s_d values.

The observed regularities are well understood after a more detailed analysis of the etching process. As described above, the formation of silicon acid H_2SiF_6 occurs in two steps [8]:

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O\,, \qquad (5)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O\,. \qquad (6)$$

However, in these reactions the crucial and yet unresolved step is oxidation of Si by nitric acid. On the one hand, recent studies have shown [8] that during the etching in acid mixtures, the injection of holes into semiconductor valence band occurs due to reduction of nitric acid on Si surface. This process indicates the electrochemical origin of the reaction. In HF–HNO_3 mixtures the electrochemical origin of etching process is confirmed by the formation of porous Si layers [9]. On the other hand, the presence of several combined equilibria between different nitrogen oxides was proposed [5] to lead to the formation of nitrous acid as a reactive species in the etching process (3), (4). Indeed, the best morphology of Si surface was obtained in HNO_3-rich HF / HNO_3 / CH_3COOH solutions, in an apparent agreement with this mechanism [5]. However, this mechanism does not explain how nitric acid is reduced on Si (111) surface passivated by hydrogen [10].

On the basis of considerations presented above, it is reasonable to assume that (i) nitric acid, as oxidizing agent, generates two holes and oxidizes the surface Si atoms to Si^{2+} according to chemical reaction and (ii) fluoric atoms replace hydrogen atoms on H-passivated Si surface in accordance with electrochemical mechanism [11].

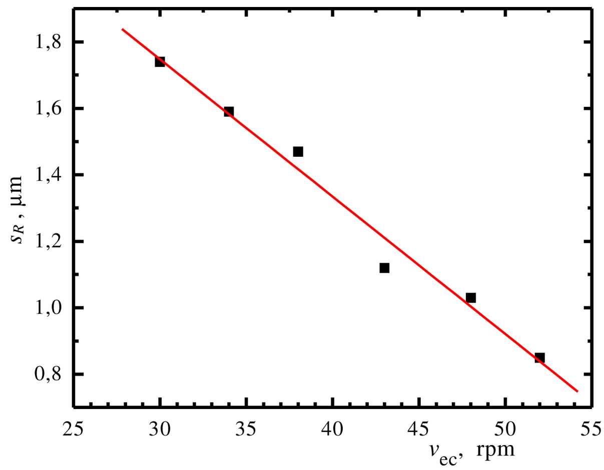


Fig. 3. Dependence of the standard deviation of the depth range s_R on the rotation rate of etching cell v_{ec} at a constant depth $d = 100$ μm of isolation grooves.

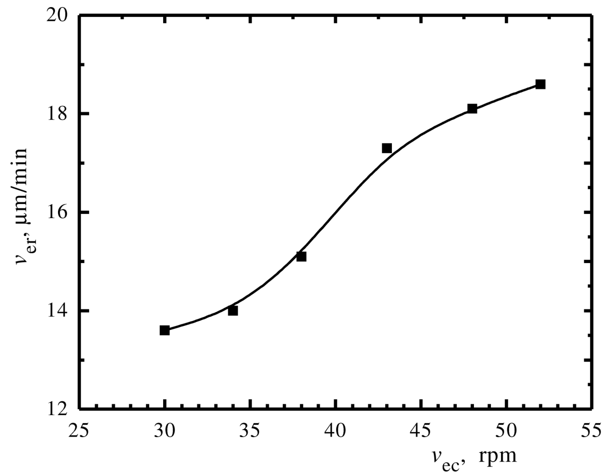


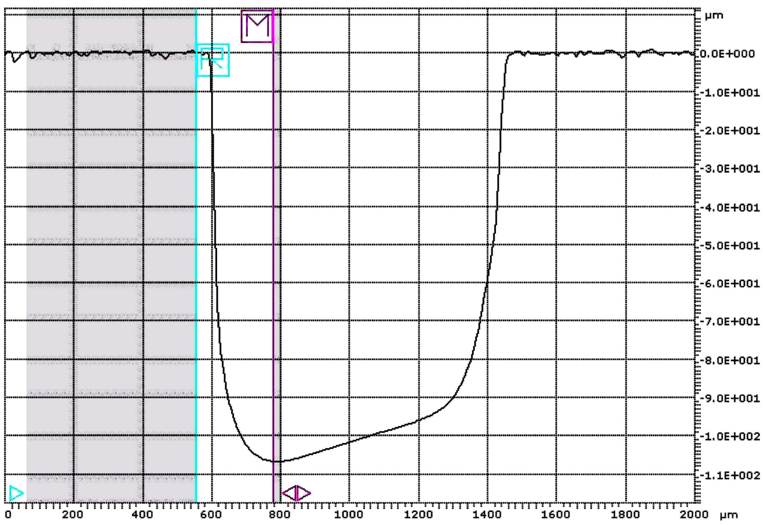
Fig. 4. Dependence of etching rate v_{er} on the rotation speed v_{ec} of etching cell at a constant depth $d = 100$ μm of isolation grooves. The curve is a guide to an eye.

As noted above (see Fig. 2), experimental data have shown that standard deviation of the depth of isolation grooves is almost constant in the p-type Si region indicating a low etching rate. However, the etching rate is strongly dependent on carrier concentration [12] which varies by four orders of magnitude in the p-type region of high-power Si devices under consideration [13]. It is reasonable to assume that hydrogen atoms, which have originated as the reaction products, penetrate into Si during etching process and passivate dopant boron atoms leading to a formation of a high-resistivity layer. As a result, the etching rate is low, leading to low s_d values of the depth of isolation grooves. An increase of s_d values in the n-type region can be explained by increased etching rate due to the absence of hydrogen passivation effect.

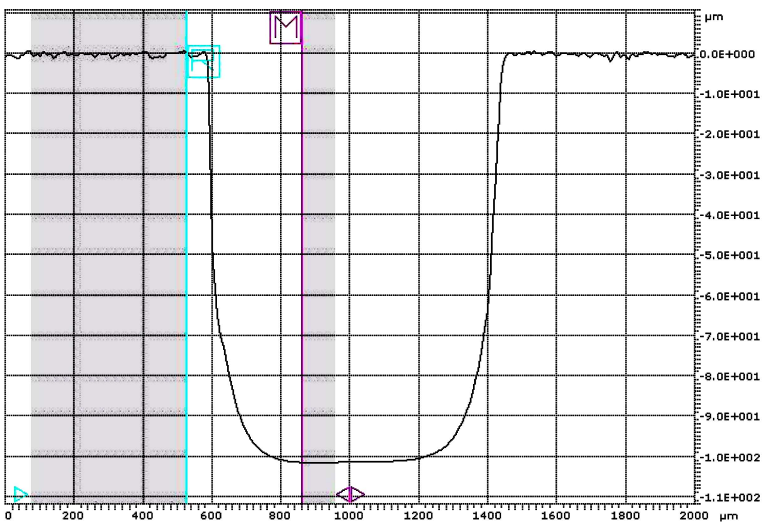
In order to decrease the range of d values over the wafer, the dependence of standard deviation s_R (the standard deviation of the depth range) on the rotation speed of etching cell v_{ec} was examined. For this purpose, the mechanism of train gears in the etching cell was improved to increase the rotation speed of the etching cell. However, the rotation speed was limited to $v_{\mathrm{ec}} < 60$ rpm because of the construction of apparatus.

Experimental data have shown (Fig. 3) that the isolation grooves are more uniform in depth at higher v_{ec} values. Therefore, it was proposed to increase the rotation speed of the etching cell up to 52 rpm. The increase of v_{ec} from 30 to 52 rpm resulted in the decrease of standard deviation of the depth range s_R from 1.74 to 0.85 μm.

The increase of rotation speed v_{ec} of etching cell resulted in the increase of etching rate, too (Fig. 4). For example, the etching rate was increased from 13.6 to



(a)



(b)

Fig. 5. Profile of the isolation grooves formed at the rotation of the etching cell with a speed of (a) 30 rpm and (b) 52 rpm.

18.6 μm/min at the increase of rotation speed from 30 to 52 rpm. This dependence is caused by the enhanced homogeneity of the etchant and a more efficient removal of reaction agents at the local wet etching process. As a result, the etching rate was increased and it was more homogeneous over the wafer.

The increase of v_{ec} has also resulted in the improvement of the profile of isolation grooves. As seen from Fig. 5, the bottom of the isolation groove is smoother at higher rotation speed of the etching cell. The improvement of morphology is mainly due to an easier removal of the reaction products.

5. Summary

The formation of isolation grooves by wet chemical etching has been investigated in the case of high-power Si devices produced by means of industrial etching apparatus in order to improve the efficiency of this step in the technological procedure. Two problems in the etching process have been discussed. The first problem was related to the chemical composition of the etching solution. It has been shown that using the HNO_3-rich $HF/HNO_3/CH_3COOH$ etchant for Si (111), the combined electrochemical and chemical reaction under hydrogen evolution is dominant. As a result, the etching rate is weakly dependent on the doping rate in p-type Si. The second problem under consideration was the etching rate and removal of reaction products from the forming isolation grooves. The standard deviation in the depth of isolation grooves was determined to decrease with the increase of rotation speed of the etching cell due to a more efficient removal of the reaction products. As a result, the profile of the isolation grooves was smoother at a higher rotation rate.

Studies of the etching process in fabrication of high-power Si devices have given a new insight into reaction mechanism of isotropic acidic etching of Si. An improvement of technology has led to lower values of standard deviation for the depth and smoother profile of isolation grooves in Si substrates.

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DIDELĖS GALIOS SILICIO PRIETAISŲ IZOLIAVIMO GRIOVELIŲ CHEMINIS ĖSDINIMAS

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Santrauka

Nagrinėjamas izoliacinio griovelio gylių verčių kitimo intervalo ir jų standartinio nuokrypio mažinimo metodas didelės galios silicio prietaisuose. Nustatyta, kad gilėjant izoliaciniams grioveliams kartu auga standartinis nuokrypis. Izoliacinio griovelio gylių verčių standartinis nuokrypis sumažintas nuo 1,74 iki 0,85 μm, didinant ėsdinimo kasetės sukimosi greitį ėsdiklyje nuo 30 iki 52 aps/min. Nustatyta, kad kartu pakito ir ėsdinimo greitis nuo 13,6 iki 18,6 μm/min. Ištirta ėsdinimo kasetės sukimosi greičio įtaka izoliacinio griovelio dugno formai ir morfologijai.