

ELASTIC REFLECTION SPECTRA ON POROUS p-TYPE SILICON LAYER  
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PSL samples have been formed on p type Si(100) wafers by an electrochemical procedure. The dependence of the elastic electron reflection coefficient,  $r_e(E)$ , on porosity ( $P$ ) was determined by elastic peak electron spectroscopy (EPES). The spectra were measured in absolute units (%) with a retarding field analyser and spectrometer corrections. They exhibited systematic decrease of intensity with porosity. HF treatment of samples produced a dramatic decrease of  $r_e(E)$  in the low energy (40-100 eV) range, due to removal of the native  $\text{SiO}_2$  and formation of Si-H bonds on the surface. It can be explained by multiple elastic reflection and attenuation of electrons by H adatoms on the pore walls. The contribution of pores to  $r_e(E)$  was considerable and increasing with porosity. The porous layers and interfaces have been studied by Auger electron spectroscopy (AES) with  $\text{Ar}^+$  ion bombardment depth profiling of high resolution.

## 1. Introduction

A comprehensive review was published on porous silicon layers (PSL) formed by anodization of Si substrates by Smith and Collins [1] in 1992. Recently, elastic scattering of electrons on PSL was studied [2-4]. This paper is confined to effects of porosity,  $P$ , i.e. the volume % of voids, covering the  $P = 47 - 78\%$  range.

In Ref. 1, preparation processes of PSL are described in details. In our present work, PSL samples were formed on p-type Si(100) wafers ( $3 \Omega\text{cm}$ ) and were implanted by 40 keV  $\text{B}^+$  ions on their backside to improve the contacts [4]. The values of  $P$  have been controlled by the composition of the electrolyte. The current density was varied between 20 - 50  $\text{mA/cm}^2$ . PSL samples of thickness  $d = 0.5 - 3 \mu\text{m}$  have been formed by controlling the anodization time. The specific surface of the samples varied between 600 - 900  $\text{m}^2\text{cm}^{-2}$  [1,4].

## 2. Experimental procedures and results

The elastic reflection coefficient,  $r_e(E)$ , was determined in absolute units (%): the percentage of elastically reflected electrons collected within the angular range ( $\theta = 125 - 175^\circ$ ) of the retarding field analyser (RFA, Riber OPR 304) [5,6]. The coefficients  $r_e(E)$  were measured by elastic peak electron spectroscopy (EPES) [5], and deduced from the elastic peak half area above the primary energy  $E_p$ , compared with that of primary electrons repelled to the grids by the biased sample [6].  $\Delta E$  modulation 0.8 V pp was used. The EPES measurements were carried out with an electron beam of  $I_p = 0.5 \mu\text{A}$ ,  $\phi = 0.7 \text{ mm}$  [3]. The surface of as received samples was covered by native  $\text{SiO}_2$  of 1-2 nm thickness. It was removed later by HF treatment. After HF etching and rinsing, the samples were introduced into the UHV chamber and pumped to  $10^{-7}$  Pa pressure. They have been subjected to cleaning by a slight  $\text{Ar}^+$  ion bombardment to remove C from the surface. AES depth profiling was carried out in a dedicated device [7], applying specimen rotation and glancing angle of incidence. The ion energy was 1 keV.

Experimental results are presented in Figs. 1-4. In Fig. 1 the elastic reflection coefficients,  $r_e(E)$ , are presented for three values of  $P$ .  $r_e(E)$  values decrease with increasing porosity. In Fig. 2 the effects of HF treatment, decreasing  $r_e(E)$  coefficients are characterized by an electron-energy ( $E$ ) dependent attenuation factor,  $\beta$ , the ratio of  $r_{eH}$  and  $r_e(E)$  coefficient after and before HF treatment:  $\beta(E) = r_{eH}/r_e(E)$ .

In Fig. 3, the electron elastic reflection coefficient,  $r_e(E, P)$  is presented for two values of  $E$ , 100 and 150 eV, and plotted versus  $P$ . In the figure two "fictive" straight lines are shown, too. They show the elastic reflection coefficient of the intact surface area of HF treated Si [2]. The pores, or voids occupy  $P$  % area, due to the thickness of the porous layer. Experimental  $r_e(E, P)$  points are above the straight lines.

*Fig. 1. Variation of elastic reflection coefficient,  $r_e(E)$ , with the porosity  $P$ .*

*Fig. 2.  $\beta(E)$  attenuation spectra, characteristic for HF treatment and H adatoms (right).*

In Fig. 4, typical AES depth profile of PSL is presented, measured on a 0.5  $\mu\text{m}$  thick PSL with  $P = 78\%$ . This displays the Auger intensities (AP PH) for the Si (92 eV), Si (78 eV, with oxygen bond) and O (510 eV) versus sputtering time. After removal of the PSL, large rise of Si peak of substrate is observed.

Experimental results can be understood taking into consideration the porous structure of layers. Unfortunately, very few transmission electron microscope (TEM) micrographs are available in the literature. In Ref. 1, the sponge-type structure of PSL formed on p Si substrate was described. A qualitative model is given below, assuming that the intact surface of the PSL behaves like a Si surface. The decrease of  $r_e(E, P)$  coefficients with  $P$  corresponds to this approach, but the contribution of the voids is important, too. The attenuation parameter  $\beta(E)$  can be explained by a simplified model, taking into consideration processes produced by HF treatment:

- HF treatment is removing the native  $\text{SiO}_2$  surface layer and producing H adatoms.

- $\sigma_{effH} \approx 2 \times 10^{-2} \sigma_{effSi}$ , i.e. the elastic reflection on the H adatoms can be neglected with respect to the Si substrate [2].

- H adatoms attenuate electrons reflected on the Si substrate in the low energy  $E < 100$  eV range by a factor  $\alpha^2 = 0.8$ .  $\alpha^2$  is a decreasing function of  $E$ .

- For low energy,  $E < 100$  eV, electron reflections on the substrate surface are dominating. Above 200 eV, electron reflections on the deeper Si atomic layers occur.
- Within the voids, multiple elastic reflection and attenuation by the H adlayer occupying also the void walls are taking place.

*Fig. 3. Elastic reflection coefficients,  $r_e(E)$ , for  $E = 100$  and  $150$  eV, plotted versus porosity ( $P$ ). They are above the “fictive” straight lines characterizing elastic reflection of the intact Si surface area, not covered by voids.  $r_{ef}(E) = (1 - P/100)r_{eSi}(E)$ .  $r_{eSi}(E)$  was measured with a HF treated Si wafer.*

*Fig. 4. Characteristic AES depth profile of a  $P = 78\%$  PSL sample, displaying Si, Si with O bond and O (right).*

All these effects affect the  $\beta(E)$  attenuation factors. In Fig. 2, they approach a constant value above 200 eV. Regarding the experimental values of  $r_e(E, P)$  shown in Fig. 3, the elastic reflection can be described by :

$$r_e(E, P) = (100 - P) \{ N_{Si} \sigma_{effH} + \alpha^2 r_{eSi} \} + P \Delta r_{eP}(E, P).$$

The first term describes the contribution of the H adatoms. It is negligible in comparison with the second term that describes the contribution of the Si substrate, including attenuation factor  $\alpha^2$  of reflected electrons.  $N_{Si}$  is the density ( $\text{cm}^{-2}$ ) of Si atoms on the surface.  $100 - P$  is the area of intact Si. The third term is the contribution of multiple elastic reflection within voids. It becomes more important with increasing  $P$ .

### 3. Conclusion

The elastic reflection spectra of porous silicon layers (PSL) sample exhibit marked change with porosity, decreasing  $r_e(E, P)$  with  $P$ . The contribution of voids in  $r_e(E, P)$  increases with  $P$ .

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#### ELASTIČNO RASPRŠENJE ELEKTRONA OD POVRŠINE POROZNOG SLOJA SILICIJA p-TIPA

Uzorci slojeva p-silicija načinjeni su na Si(100) pločicama elektrokemijskim postupkom. Metodom elektronske spektroskopije za elastično raspršenje, određena je ovisnost elastičnog refleksijskog faktora,  $r_e$ , o poroznosti uzorka. Refleksijski faktor se smanjuje s povećanjem poroznosti. Jetkanje uzoraka s HF snažno je smanjilo  $r_e$  za niske energije elektrona (40 - 100 eV) zbog uklanjanja SiO<sub>2</sub> i stvaranja Si-H vezanja na površini. Porozni slojevi i granice proučavani su Augerovom elektronskom spektroskopijom, primjenom snopa Ar<sup>+</sup> i dubinskog određivanja profila uz visoko razlučivanje.