

Investigation of different oxidation processes for porous silicon studied by spectroscopic ellipsometry

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Abstract

In this paper we investigate the oxidation of porous silicon by O_3 , H_2O_2 , and, for comparison, in normal air. Such an oxidation may serve as passivation for porous silicon in applications in order to prevent devices from degradation.

The changes in the dielectric function caused by this oxidation was monitored by spectroscopic ellipsometry. Application of both H_2O_2 and O_3 resulted in a significant lowering of the values of the imaginary part of the dielectric function as expected when oxidizing the inner surfaces of these layers. For a multilayer structure we show that ozone treatment of this structure indeed passivates that sample against further oxidation in air as studied over an extended period of time (3 months).

Keywords: Oxidation; Silicon; Ellipsometry; Multilayers

1. Introduction

Surface passivation is a prerequisite for many device applications. Otherwise degradation of the device performance might occur. This is a particular problem with devices made from porous silicon, because the inner surface is very large. In porous multilayer structures designed to function as optical filters the oxidation in air of the inner surfaces changes the dielectric function of the layers and therefore the transmission wavelength would change with time.

One solution to this problem is a passivation of porous silicon layers in a rapid thermal oxidation (RTO) process using oxygen at temperatures above 900 °C. The advantage of this process for p-type material is that the photoluminescence (PL) intensity increases [1]. For many applications, however, high-temperature steps which might possibly change the microstructure [2] must be avoided. A passivation process which uses much lower temperatures is therefore needed. Here, we report on the applicability of ozone (O_3) and hydrogen peroxide H_2O_2 . Both chemicals are strong oxidizing agents and already oxidize silicon at room temperature [3,4]. The results obtained here are compared with oxidation in normal air.

2. Experimental

In this study we investigated two different types of samples: (i) porous single layers on silicon substrates and (ii) multilayer samples consisting of alternating porous silicon layers with different porosities and thicknesses.

The single layers were prepared in the dark by anodically etching of p-type Si ($0.2 \Omega \text{ cm}$) in a mixture of 50% HF and C_2H_5 1:1. The current density was chosen to be 40 mA cm^{-2} and the total etching time was 210 s. This is expected to result in a porosity of 65% and a layer thickness of 5 μm .

The multilayer sample was etched with periodically switching current densities from a p-type ($0.2 \Omega \text{ cm}$) silicon wafer. It consisted of ten alternating layers with porosities of 62% and 75% and thicknesses of 97 nm and 128 nm respectively.

The samples were characterized by a conventional rotating analyzer ellipsometer in the spectral range 1.8–5.5 eV directly after preparation, after storage in N_2 or air, and during and after further treatments with O_3 and H_2O_2 . All spectra and time-dependent measurements were interpreted in terms of the effective dielectric function $\langle \epsilon \rangle$.

Oxidizing the porous silicon layers was performed in the following.

1. A mixture of H_2O_2 , C_2H_5 and water. The concentrations and the etching time were the parameters varied in this study. The spectra were measured in ambient air directly

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after removal of the samples from the H_2O_2 solution and drying the samples by blowing with dry nitrogen.

2. An ozone atmosphere. After preparation the samples were kept in a N_2 atmosphere. For monitoring the passivation process the samples were introduced into an ozone box with optical windows. Ozone was produced inside the box from pure oxygen illuminated with UV light. The temporal evolution of the effective dielectric function $\langle \epsilon \rangle$ of the layers during passivation was measured at one wavelength (4.13 eV and 4.25 eV respectively). In order to obtain more information about the samples, spectra were also taken during the process. For the single layers the samples were kept in a N_2 atmosphere while taking spectra. Ozonisation of the multilayers was not stopped during spectral measurements since the ellipsometer used for these measurements was very fast.

3. Results and discussion

The effect of H_2O_2 on $\langle \epsilon \rangle$ of porous silicon (65%, 5 μm) is shown in Fig. 1. For photon energies below 3 eV the light penetrates into the underlying silicon substrate indicated by the interference features not fully resolved by the measurement. Above approximately 3 eV only the layer properties are probed. A single feature around 4.3 eV in $\text{Im}\langle \epsilon \rangle$ which is related to the E_2 interband critical point of bulk silicon and a shoulder at approximately 3.7 eV are visible. The latter feature is likely related to the E_1 or E_0' interband critical points of silicon [5]. This feature indicates percolation as discussed elsewhere in another publication [6]. These spectra are typical for porous layers formed on low-doped material [7].

The effect of oxidation is an overall reduction in the imaginary part of the dielectric function. Since silicon oxides are mainly transparent in the spectral region considered here and their values of the refractive index ($n=2$) are much less than that of bulk silicon ($n=4$) this behaviour during the ozonisation is expected. Note that the lineshape of $\text{Im}\langle \epsilon \rangle$ is hardly affected by the oxidation process and the spectral location of

the feature at 4.4 eV does not change. Because of the dependence of electronic transition energy on crystallite dimension [8] this indicates that the crystallite size distribution in the layers is not changed by the oxidation. Therefore it can be concluded from the strong reduction of $\langle \epsilon \rangle$ in Fig. 1 that H_2O_2 treatment leads to strong oxidation of the porous layers.

In contrast, the oxidation in normal air is very slow but shows the same spectral behaviour as seen in Fig. 1, and therefore is not separately shown here. Oxidization of a sample in normal air for a couple of days would result in a similar effect on $\langle \epsilon \rangle$ as exposing the sample to H_2O_2 for 1 min. This agrees with the idea that the inner surfaces are terminated with hydrogen after etching with HF which is known to protect bulk silicon surfaces for a couple of days [9].

Fig. 2(a) shows the evolution of $\langle \epsilon \rangle$ during ozone treatment of a single layer with 65% porosity and 5 μm thickness. The oxidation proceeds quickly in the first hour and slows down afterwards.

In Fig. 2(b) spectra taken during ozone treatment of a porous silicon layer at times denoted by (●) in Fig. 2(a) are shown. Similar features as for H_2O_2 treatment can be observed. But the reduction in $\langle \epsilon \rangle$ for these layers is stronger than for H_2O_2 treatment (Fig. 1). The large change of the values of $\text{Im}\langle \epsilon \rangle$ reveal that not only the surface but fairly the whole layer is oxidized after ozone exposure for 20 h.

The slightly different absolute values and spectral positions of $\langle \epsilon \rangle$ in Fig. 1 and Fig. 2 are due to the fact that the sample shown in Fig. 1 had a somewhat higher porosity and different microstructure as a result of little white light illumination during preparation [10].

In contrast to the single layers, the multilayered samples show quite different spectral behaviour due to interferences in the layers. In the following section we discuss measurements on multilayer samples designed as Fabry Perot filters with a transmission wavelength of about 1.5 eV. Once again, first the ozone exposure was monitored at 4.25 eV as shown in Fig. 3. At this photon energy the penetration depth of light is very small (less than 100 nm). Hence, only the topmost layer is probed. For multilayer structures the effective dielectric function reveals features due to interferences within the

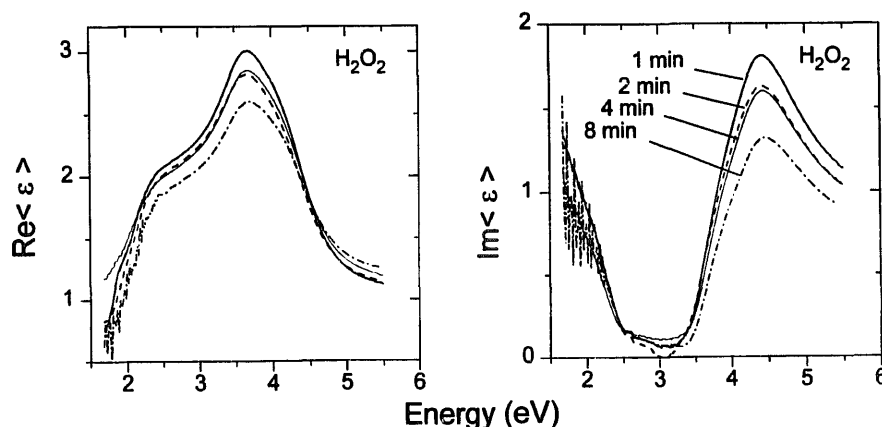


Fig. 1. $\langle \epsilon \rangle$ for a single-layer porous silicon sample. Shown is the real and imaginary part after treatment with 30% $\text{H}_2\text{O}_2 + \text{C}_2\text{H}_5$ 1:1 for different time periods

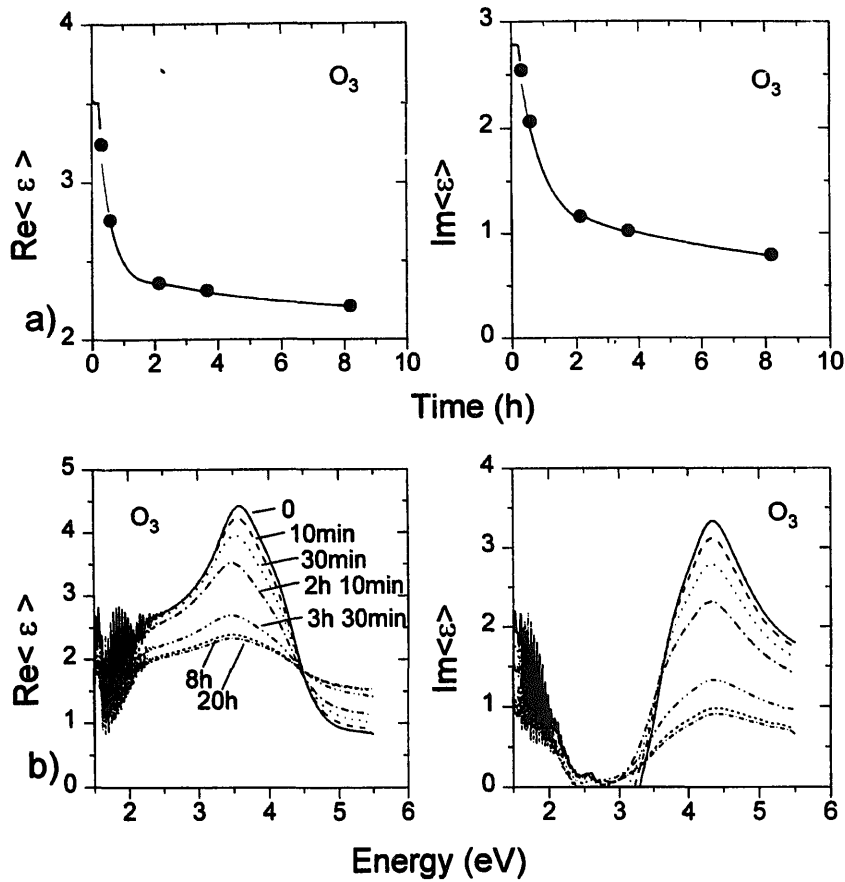


Fig. 2. (a) Time development of $\langle \epsilon \rangle$ at 4.13 eV during oxidation a single layer in an ozone (O_3) atmosphere. At the points marked by (●) spectra are taken. (b) Spectra of $\langle \epsilon \rangle$ after various ozonization times. The spectrum taken after 20 h of ozone treatment does not change any more even for longer times of ozonisation.

layers as can be seen in Fig. 4 at approximately 2.5 and 2.3 eV for the untreated sample. The main interference at about 1.5 eV is much stronger and sharper, but was outside the spectral range of the ellipsometer. These features in the dielectric function are correlated with maxima and minima of the reflectance (see Fig. 5). During ozone treatment the spec-

tral position of this interference feature shifts towards higher energies due to the change of the dielectric function and therefore change of refractive index of each single layer by oxidation. Further storage of the sample for three months in air causes only a small change of the dielectric function. We assume that in this case the layers are not fully oxidised. For single layers a full oxidation was already observed after about 20 h of ozone treatment. So the observed additional spectral shift after further storage in air for the multilayered sample might vanish after longer ozone treatment.

4. Summary and conclusions

The effect of oxidation by ozone and H_2O_2 on the dielectric function of porous silicon was studied. Since the oxidation rate of porous silicon in air and O_3 is small, the process can easily be monitored by spectroscopic ellipsometry.

Oxidation in H_2O_2 is very fast but results only in thin oxide layers. In contrast, with O_3 , oxide layers several nanometres thick can be formed. Structures oxidized by ozone, moreover, will be stable in an environment of normal air. Therefore, ozone is very well suited for a passivation of porous silicon layers. Since the oxidation rate by ozone is much higher than

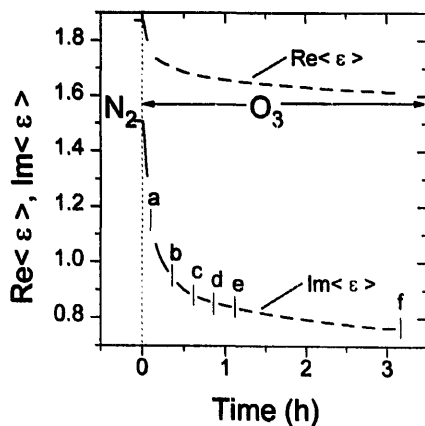


Fig. 3. Evolution of $\langle \epsilon \rangle$ at 4.25 eV of the multilayer sample during ozone treatment. At the beginning the sample was kept in a N_2 atmosphere. After starting ozone treatment at $t=0$ h $\langle \epsilon \rangle$ decreases rapidly. Every few minutes a spectrum was taken in an ozone atmosphere (a–f).

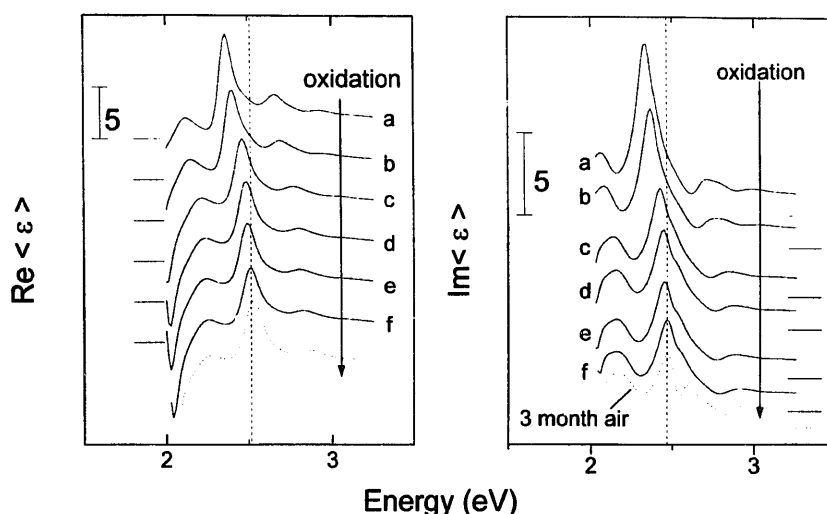


Fig. 4. The effective dielectric function of a porous silicon multilayer during oxidation in O_3 measured at the times indicated in fig. 3. Corresponding zeros are indicated by horizontal lines. The spectral shift of the interference structures of the layers can clearly be seen. The dashed spectra are taken after further storage in air for 3 months. In the beginning of oxidation the peak shifts to higher energies. After about 3.5 h of oxidation the peak position is fixed and remains stable for at least 3 months (2 200 h).

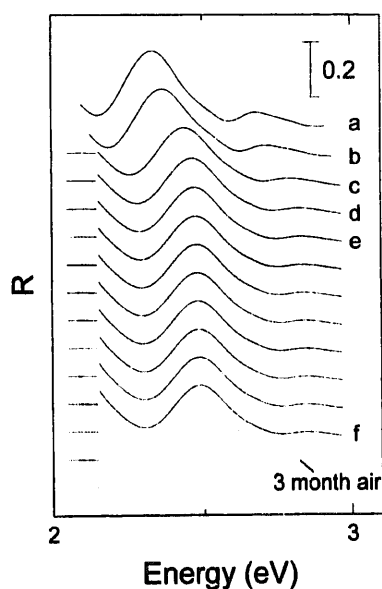


Fig. 5. Reflectivity with corresponding zero lines calculated from the spectra shown in Fig. 4. In the beginning of oxidation the peak at about 2.3 eV shifts to higher energies. After about 3.5 h of oxidation (f) the peak position is fixed and remains fairly stable for at least 3 months in normal air.

that by normal air this oxidation process will also allow aging of the layers to be studied.

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