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Non-destructive Spatially Resolved Characterization of Porous Silicon Layer Stacks

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Abstract. Porosity and thickness of porous silicon layers, enabling the layer transfer process, are very important quantities to control reorganization of pores from the as-etched state to serving as seed layer for high quality epitaxy and predetermined breaking points for epiwafer detachment. Gravimetric determination of porosity allows only determining mean values, and those even only for single but not double layers. In addition, the method is destructive. In contrast, fitting of the optical reflectance of the porosified Si wafer allows getting these layer characteristics in a non-destructive way. We present here a characterization method based on reflectance measurements and a robust exploitation algorithm, which allows for the accurate determination of thickness and porosity of single and double porous layer stacks in a non-destructive way. Taking reflectance spectra spatially resolved allows therefore obtaining both porosity and thickness values with the same resolution. As an example, this method is used here to extract correlations between local porosity and local etching rate that are consistent with known dependencies between porosity and etching current.

INTRODUCTION

Interest in exploiting porous silicon (PS) industrially has recently gained importance with applications such as sensors, anodes in lithium-ion batteries, in microelectronics, and for photovoltaics [1]. For example, PS is used as the seed and detachment layer in the epitaxial layer transfer process for the fabrication of silicon thin films or 'EpiWafers' [2]. This provides an effective alternative to significantly reduce the cost of the silicon wafer as well as the CO_2 footprint, because wafers are grown directly from silanes instead of melting and crystalizing Si ingots, and the porous substrate wafers are re-used while minimizing kerf-loss.

In the layer transfer process, the silicon is usually grown epitaxially on multi-layer reorganized PS via a chemical vapour deposition (CVD) process. The structural properties of the porous layers such as shape, pore diameter, porosity, and thickness influence the reorganization process [3] and thus the seed layer for subsequent epitaxial silicon growth. These properties can be tuned during the electrochemical anodization of the silicon to form PS by adjusting the etching parameters. The porosity and the thickness of PS are usually determined via a gravimetrically weighing of the sample before and after porous Si etching and finally after removing the porous layer in an aqueous KOH solution. This method is, however, destructive and the estimated porosity and layer thickness are mean values for a larger area. The determination of the local porosity on small area ($<1\ cm^2$) of a large M2 wafer is gravimetrically rather not possible even with high precision balances due to the large weight of the wafer compared to the small weight of the PS layer. It is therefore of high interest to determine these quantities from optical measurements which do not present the aforementioned limitation. Additionally, the layer transfer process implies the porosification of a two-layer stack on which the gravimetric method is completely inapplicable. In this case, that is even more relevant for the layer transfer process, the suitable fitting of the optical measurement allows the determination of thickness and porosities for both layers.

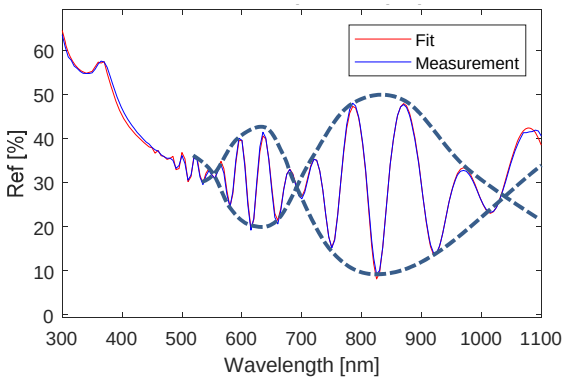
OPTICAL MODELING

The sample is modelled as 1 or 2 PS layer system on crystalline silicon where each layer is defined by its thickness *d* and its optical constant. The optical constants of PS are linked to the layer porosity *P* using the Bruggeman effective media approximation (EMA) [4]. A roughness parameter *s* is used to describe the interface between the wafer and the layer. The reflectance is calculated using the transfer matrix method using *d*, *s* and *P* as fitting parameters.

While the average level of the spectrum determines mostly the porosity (the higher the average level, the lower the porosity), the frequency of the interference pattern determines then the layer thickness (the higher the thickness, the higher the frequency). For given porosity and thickness, the amplitude of the oscillation then determines the interface roughness.

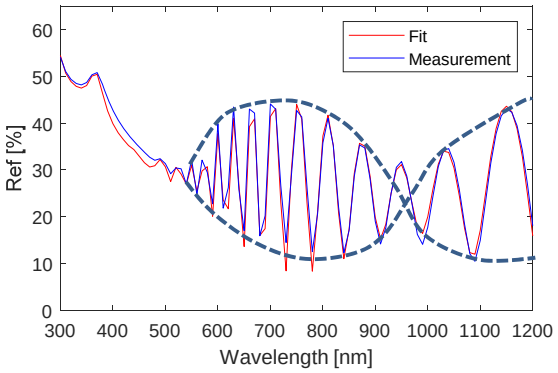
While in a single layer system there is an oscillatory interference pattern in the measured reflectance spectrum, in a two-layer system there is a beat where the envelope frequency and the internal frequency are characteristics of the thicknesses of each layer.

Taking advantage of the possible partial decoupling of the influence of each fitting parameter (6 parameters: *d*, *P*, and *s* for the 2 layers) on spectrum shape amplitude etc., we developed an algorithm that fits very robustly a large variety of layer combinations quasi automatically and with minimal prior knowledge of the layers.



(a)

	Top layer	Bottom layer
d (nm)	910	490
P (%)	17.5	54
s (nm)	19.5	30



(b)

	Top layer	Bottom layer
d (nm)	1464	268
P (%)	24.4	59
s (nm)	22	30

FIGURE 1. Examples of two double layer reflectance spectra with beat frequency sketched in dashed, with their fitting parameters.

We see in Fig. 1 two examples of fittings performed with the algorithm where we see that for the beat, frequency and amplitude fit and measurement agree.

One can see that the beat frequency is higher for stack (a) than for stack (b), which indicates that its top layer is thicker. However, its inner frequency is smaller indicating that the bottom layer is thinner.

The fitting conditions are the best when the beat is well identified. This requires that the two layers have significantly different porosities (like in Fig. 1: 20% vs. 60%), a significantly different thickness (typically factor 2) and a moderate roughness for the interface between both layers.

The fitting procedure developed is, however, successful even when the two layers are of the same order of thickness and not too different concerning porosity, provided the starting parameter values for the algorithm are closer to the expected ones.

This method allows determining a large range of porosity (0-90%) and as well as thickness (10 nm – 10 µm).

SPATIALLY RESOLVED THICKNESS AND POROSITY

An automated system for reflectance measured on an xy-table allows to measure on each sample 25 x 25 reflectance spectra from 300-1200 nm. With the algorithm developed for single spectrum fitting and taking advantage of the continuous spatial evolution of each parameter, a robust and quasi automated fitting procedure of all spectra of a wafer is performed allowing for the mapping of thickness and porosity of both layers over the whole porosified wafer surface.

We see in Fig. 2 the mapping of thickness and porosity of a PS layer stack used for the layer transfer process where the top layer is thick and has low porosity while the bottom layer is thin and has a higher porosity.

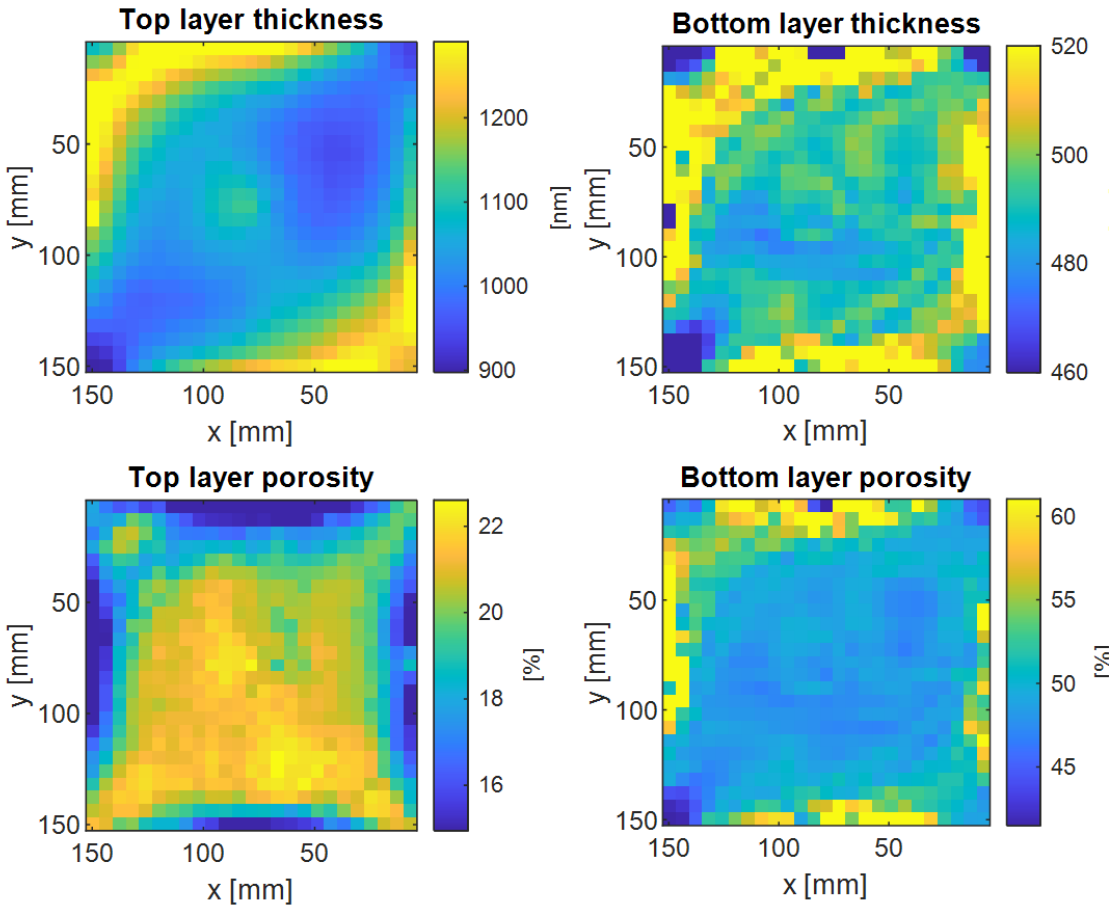


FIGURE 2. Distribution of thickness and porosity for a stack of low porosity layer (LPL) at the top and high porosity layer (HPL) at the bottom.

This technique allows the detection of complex distribution patterns between the thicknesses and porosities of the two layers, which could be for the first time carefully investigated.

We see for example in Fig. 2 that regions at the edge close to the top left and bottom right corners are thicker for top and bottom layer than in the centre. This could be explained by an inhomogeneous current distribution in the etching basin due to basin or electrode characteristics, geometry etc. that could be further investigated if required in order to increase the layer homogeneity.

We see that this thicker region is also more porous for the bottom layer. This might be explained by the well-known fact that increasing the current density, which increases the layer thickness, also increases the porosity [5] (also shown locally for single layers in the next section). More surprising is the fact that regions of low porosity of the top layer are of high porosity for the bottom layer and vice versa. An increased current density leading to a

decrease in porosity is never observed for single layers regardless of current density time electrolyte composition doping etc. This shows that etching the bottom layer is influenced by the presence of the top layer and also may change slightly the top layer properties. This can be for the first time carefully investigated.

For some single layers, the mean values of thickness and porosity fitted for all measured points of the wafer were compared to gravimetric measurement of an identically processed wafer. One can see in Tab. 1 that both methods are in agreement.

TABLE 1. Comparison between gravimetric and reflectance fitting method for 2 single layers

	Layer 1 Reflectance	**Layer 1 Gravimetry**	**Layer 2 Reflectance**	**Layer 2 Gravimetry**
d (nm)	3705	3931	3012	3093
P (%)	33.8	32.9	55.3	55.4

STATISTICS AND CORRELATION BETWEEN LOCAL THICKNESS AND POROSITIES

It is well known that for a given electrolyte composition and substrate doping, the porosity of a layer is a function of the etching current density. This relation was up to now only shown with average porosity values determined by gravimetry and an average current density applied to the full wafer [5]. This is expected to hold also for regions as small as the spot size of the reflectance setup used in this study (some mm^2), because the etching process occurs on thicknesses of only 1-3 µm.

While the porosity can be evaluated locally, the local current density is not directly accessible. One can, however, evaluate locally the effective etch rate ($P \cdot d / t_{etch}$), that is the volume of silicon etched per second and per unit area. At not too high current and/or too diluted etching solution, the amount of electrons necessary to etch one silicon atom, the valence, is rather constant [6]. In these circumstances, the local effective etch rate can be used as a measure of the local current density because they are simply proportional to each other.

We etched samples with various currents and mapped their layer thickness and porosity using the presented technique. The local effective etch rate (as an image of the local current density) is represented as function of the local porosity in Fig. 3. A clear and continuous correlation between the two parameters is observed independently of the etching condition of the respective sample.

In addition, it needs to be mentioned that samples etched at 4 mA/cm^2 using two different etching times show almost the same porosity distribution versus the effective etch rate, demonstrating the independence of this relation on the etching duration in the investigated parameter range.

In conclusion, the spatially resolved measurement of porosity and thickness allowed showing this correlation clearly, confirming that it also holds locally on the wafer as supposed.

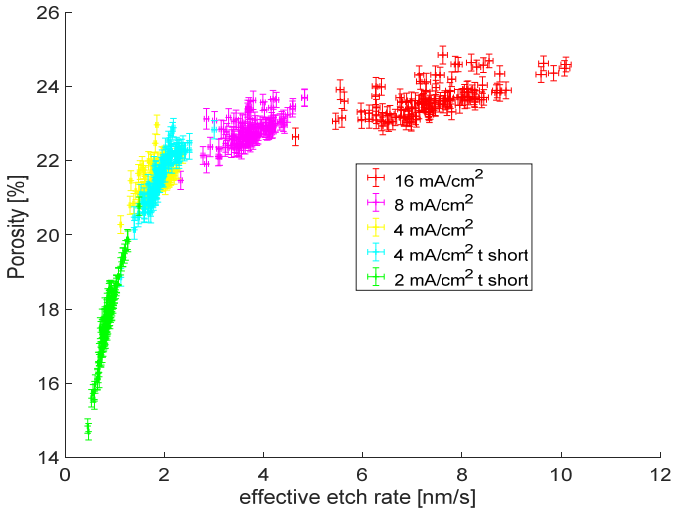


FIGURE 3. Porosity as a function of the effective etch rate for each measured point on the wafer and investigated layer.

CONCLUSION AND OUTLOOK

We presented a method that allows for the non-destructive and spatially resolved determination of the thickness and porosity of single/double layer porous silicon stack. This method is based on the fitting of reflectance spectra using a robust and quasi automated procedure. It allows determining porosity over a very large range (0-90%) as well as the thickness over a large range (10 nm – 10 µm).

As an example, we showed a correlation between local porosity and local etching rate that is consistent with known dependencies between porosity and etching current.

As this method can be used on two-layer stacks on which the gravimetric method is completely inapplicable, it allows investigating the influence of the etching condition of one layer on the etching of the other layer.

With respect to more practical issues, this technique allows to correlate more directly porosity and thickness distributions to current inhomogeneity in the porosification process but also with the epiwafer detachment and/or quality in the subsequent epitaxial layer transfer process.

ACKNOWLEDGENMENTS

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REFERENCES

1. A. Ivanov, “Silicon Anodization as a Structuring Technique, Literature Review, Modeling and Experiments,” Dissertation Albert-Ludwigs-Universität Freiburg, 2016.
2. R. Brendel, Jap. J. Appl. Phys. **40**(7), 4431-4439 (2001).
3. V. Depauw, "Transferable monocrystalline thin films by annealing of macroporous silicon: Potential for solar cell applications," Dissertation, Katholike Universiteit Leuven, 2009.
4. D. A. G. Bruggeman, Annalen der Physik **24**, 636–664 (1935).
5. C. S. Solanki et al., J. Electrochem. Soc. **151**, C307-C314 (2004).
6. V. Lehmann, *Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications* (Wiley-VCH Verlag GmbH, 2002).