

OPTICAL PROPERTIES OF POROUS SILICON FILMS*

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The optical constants of porous silicon layers formed in wafers with resistivities of 0.01–25 Ω cm and densities of 20%–75% were determined by ellipsometry in the wavelength range 0.28–0.7 μ m and by reflectance and transmission from 0.6 to 2.5 μ m. The IR refractive index was found to decrease as the density was reduced and an effective medium model was used to obtain density values from the optical data. Good agreement was obtained with gravimetric densities for 0.01 Ω cm samples on the assumption of a mixture of crystalline silicon and air, but material of higher resistivity showed apparently reduced optical densities because of the presence of some oxidized silicon. The optical measurements indicate that the material is a chemical mixture (SiO_x) at high oxygen concentrations. ϵ_1 and ϵ_2 spectra showed that 0.01 Ω cm samples had better crystallinity than higher resistivity samples and this was confirmed by the observation of amorphous-like bands in photoluminescence spectra of the latter material.

1. INTRODUCTION

Oxidized porous silicon has considerable potential as the basis of a silicon-on-insulator technology for full device isolation¹. Anodization of silicon wafers in aqueous HF produces porous silicon (PS), which contains a network of pores of dimensions approximately 100 Å while still retaining, under optimum conditions, the crystallinity of the original wafer. Because of the high surface area of the porous material, PS can be rapidly oxidized to form a bulk oxide with insulating properties approaching those of thermal SiO_2 ². The structure of PS is still not fully understood and its properties are dependent on the starting material and the anodization conditions. The physical properties, such as density, of the PS films studied here have been investigated as a function of the silicon resistivity, the current density and the HF concentration³. The technologically important density is around 45% since the volume expansion on oxidation should produce a dense fully oxidized structure

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with minimal strain. The aim is to identify conditions to produce this optimum density with maximum retention of the single-crystal characteristics of the original wafer. In the present study simple optical techniques, reflectance and transmission, were investigated as a non-destructive measurement of the density, and the detailed structure of the PS was further investigated using the more sensitive optical techniques of ellipsometry and photoluminescence.

2. EXPERIMENTAL DETAILS

The production of the PS layers using a double anodization cell has been discussed previously^{3,4}. Uniform layers with thicknesses of 1–20 μm were formed in p-type boron-doped Si(100) wafers of diameter 3 in with resistivities of 0.01, 0.1, 1, 5 and 25 $\Omega\text{ cm}$. Measurements of the weight loss on anodization together with a measurement of the thickness by scanning electron microscopy on a cleaved edge were used as a gravimetric assessment of the PS density, which varied from 20% to 75% (of the bulk silicon density, *i.e.* 2.33 g cm^{-3}). Reflectance and transmission spectra were measured in the wavelength range 0.6–2.5 μm at normal incidence using a Beckman DK-2A spectrometer. Ellipsometry measurements were performed at an angle of incidence of 70° from 0.28 to 0.7 μm with an automatic wavelength-scanning nulling ellipsometer which has been described previously⁵.

3. RESULTS AND DISCUSSION

Typical interference fringes obtained from as-anodized wafers are shown in Fig. 1; these are due to reflection at the refractive index discontinuity at the interface of the PS and the silicon substrate. Both transmission and reflectance spectra were obtained for resistivities of 0.1–25 $\Omega\text{ cm}$ but for the low resistivity (0.01 $\Omega\text{ cm}$) samples free-carrier absorption in the substrate prevented any transmission.

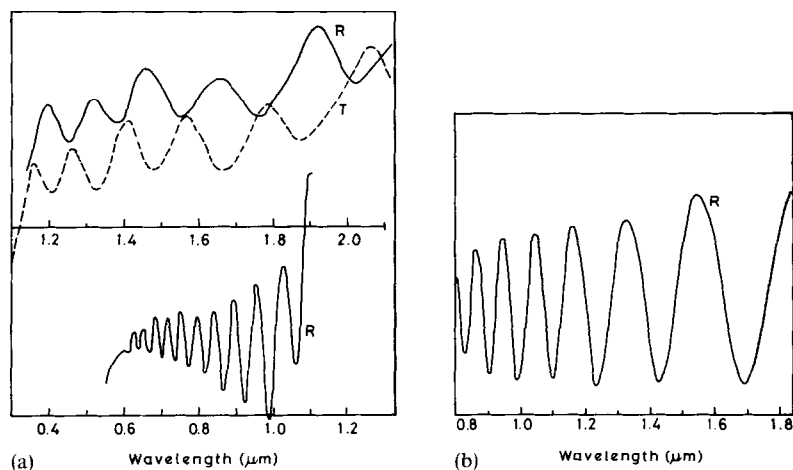


Fig. 1. Typical reflectance R and transmission T spectra of (a) high resistivity PS layers (5 $\Omega\text{ cm}$; 41%; thickness, 5.3 μm) and (b) low resistivity PS layers (0.01 $\Omega\text{ cm}$; 21%; thickness, 3.3 μm).

However, even and well-defined fringes were always observed in reflectance over a wide range of wavelengths for the latter samples (see Fig. 1(b)). The results were analysed using the equation

$$\frac{1}{2nd} = \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \quad (1)$$

where n is the refractive index, d is the layer thickness and λ_1 and λ_2 are the wavelengths of successive maxima or minima. This equation is valid for normal incidence and constant n and assumes a net phase change of 0° or 180° , conditions fulfilled for $\lambda > 1 \mu\text{m}$ where the absorption index k is approximately zero. Since d is known from a cleaved-edge scanning electron microscopy measurement, n can be obtained from the fringe separations. Figure 2 shows n as a function of wavelength for several samples of different densities. Also included in this diagram are results at shorter wavelengths obtained from ellipsometry measurements discussed later. The n values obtained from ellipsometry extrapolate smoothly into those obtained using the interference method, indicating the validity of the latter technique, particularly in the region above $1 \mu\text{m}$ where n is constant within the scatter. For PS of reducing density the IR refractive index n_{IR} can be seen to fall from the value for crystalline silicon (3.47) towards unity (air) as voids become a larger proportion of the material.

The averaged values of n_{IR} (for $\lambda \geq 1 \mu\text{m}$) were used with the Bruggeman effective medium approximation⁸ (EMA) to obtain values for the density of the PS layer. For two or more phases (a, b etc.)

$$f_a \left(\frac{\epsilon_a - \epsilon}{\epsilon_a + 2\epsilon} \right) + f_b \left(\frac{\epsilon_b - \epsilon}{\epsilon_b + 2\epsilon} \right) + \dots = 0 \quad (2)$$

where

$$f_a + f_b + \dots = 1$$

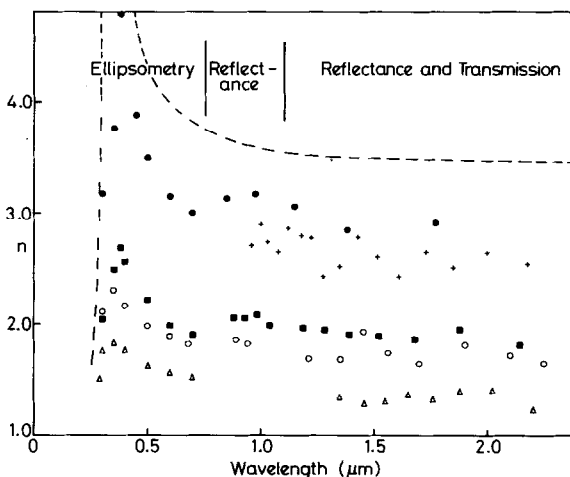


Fig. 2. Wavelength dependence of refractive index n values obtained by ellipsometry, reflectance and transmission for PS samples of various densities: ●, +, 72%; ■, ○, 45%; △, 36%; ---, data for crystalline silicon^{6,7}. n is the real part of the complex refractive index: $\tilde{n} = n + ik$.

ϵ_a and ϵ_b are dielectric constants of phases a and b and f_a and f_b are the volume fractions. For a mixture of crystalline silicon and voids in the region $\lambda \gtrsim 1 \mu\text{m}$ ($k = 0$) we have $\epsilon_a = n_{\text{Si}}^2$, $\epsilon_b = 1$, $\epsilon = n^2$, $f_a = f_{\text{Si}}$ and $f_b = 1 - f_{\text{Si}}$. Therefore from eqn. (2)

$$f_{\text{Si}} = \frac{(1 - n^2)(n_{\text{Si}}^2 + 2n^2)}{3n^2(1 - n_{\text{Si}}^2)} \quad (3)$$

The optical density values thus obtained are compared with the gravimetric densities in Fig. 3. The densities obtained by the two techniques can be seen to agree for the $0.01 \Omega \text{cm}$ samples over the complete range indicating that this material consists of mainly crystalline silicon and voids. However, the results for all higher resistivity material are scattered, with the optical density values below the gravimetric values. These reduced values can be explained if partial oxidation of the PS has occurred on anodization. Silicon oxides have a much lower refractive index (about 1.43)⁹ but have a physical density similar to that of crystalline silicon. Therefore a variable amount of oxide present on anodization would not affect the weight loss measurements used for the gravimetric density determination. Incorporation of SiO_2 as an extra phase in the EMA (eqn. (2)) would lower the effective refractive index and produce an apparently reduced density as shown for various oxide proportions in Fig. 3. The presence of oxidized silicon in the as-anodized high resistivity material but not in the low resistivity material was confirmed by oxidation experiments¹⁰. For the $0.01 \Omega \text{cm}$ samples full oxidation was obtained indicating negligible oxide content. However, for PS produced in higher resistivity substrates lower weight gains were observed indicating that partial oxidation had already occurred, up to 50% of the remaining silicon being in the form of silicon oxides. This difference in the two types of material is associated with the different pore structures observed in transmission electron microscopy experiments³. For a given density, the pores in the high resistivity material appear to be smaller than those in the $0.01 \Omega \text{cm}$ material and therefore would have a higher surface area and hence a higher probability of oxidation. The difference in oxygen content for the two types of material deduced here has been observed directly in secondary ion mass spectrometry analyses¹⁰.

Concentrations of oxide obtained from EMA calculations of the refractive index are in good agreement with those determined gravimetrically for low oxide concentrations (about 20%) but appear to be higher than expected at higher concentrations¹⁰. This discrepancy, which may indicate the form of the oxide, can be seen in Fig. 4 which shows the results of oxidation experiments on a series of samples with similar densities and resistivities. At high concentrations, the n_{IR} values fall below the curve calculated on the basis of a physical mixture of silicon and SiO_2 phases together with voids. The results are much better described by a curve based on a chemical mixture of silicon and oxygen in the form SiO_x ¹¹. This curve has been calculated using SiO_x as one phase, with refractive index values given by Wemple¹², and voids as the other phase. Some scatter would be expected because of density variations about the averaged value of 42% (*i.e.* 58% voids) used for the calculation but the refractive index values are clearly too low to be explained on the simple physical mixture model. This conclusion is supported by the ellipsometry results to

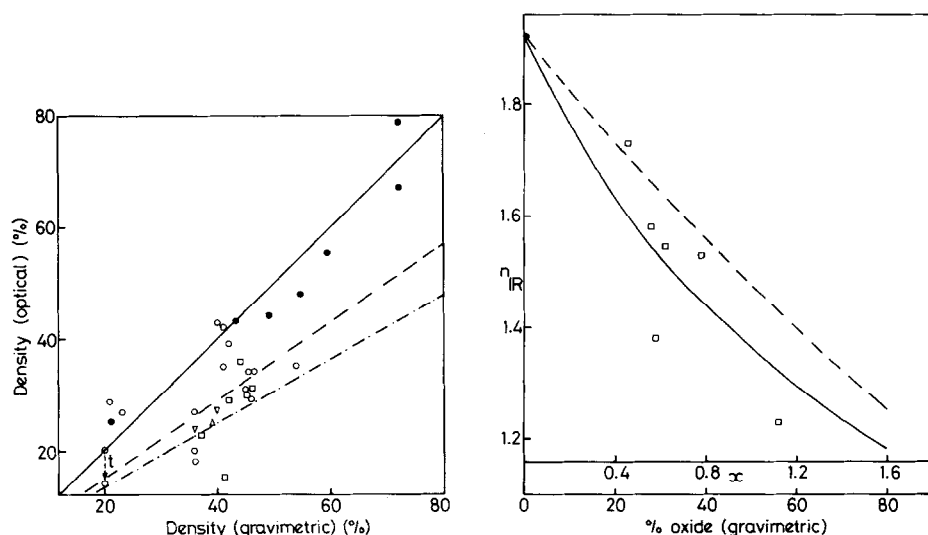


Fig. 3. Comparison of optical density and gravimetric density for PS samples of various resistivities (●, 0.01 Ω cm; △, 0.1 Ω cm; ▽, 1 Ω cm; □, 5 Ω cm; ○, 25 Ω cm): —, line of perfect agreement; ---, ---, effect on the optical density of various volume fractions $[\text{SiO}_2]/([\text{Si}] + [\text{SiO}_2])$ of oxide (---, 35%; ---, 50%).

Fig. 4. IR refractive index n_{IR} values as a function of the gravimetrically determined oxide content for PS samples of resistivity 0.01 Ω cm (●) and 5 Ω cm (□) and with similar densities (42% \pm 4%) (voids, 58%): ---, curve calculated by assuming a physical mixture of silicon and SiO_2 ; —, curve obtained on the assumption of a chemical mixture of silicon and oxygen. The x scale to be used for the SiO_x curve was calculated from the percentage oxide scale.

be discussed next and also the fact that no single-crystal features can be seen in X-ray diffraction measurements¹³ on the two samples with the lowest values of n_{IR} .

Values of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , were obtained directly from the ellipsometry measurements, treating the PS as bulk material, a valid assumption for the samples discussed here¹⁰. Figure 5 shows the variations in ϵ_1 and ϵ_2 with wavelength for typical 0.01 and 25 Ω cm samples. Spectra of high density (approximately 70%) 0.01 Ω cm samples were similar to those of crystalline silicon with a reduction in magnitude due to the presence of voids¹⁰. Spectra of the lower density samples, shown in the diagrams, exhibit a clear difference between 0.01 and 25 Ω cm samples. The 0.01 Ω cm sample shows a sharp peak in ϵ_1 close to that for crystalline silicon while the spectrum of the 25 Ω cm sample with a similar density has a broadened peak shifted to higher energy as well as a reduced overall magnitude. A similar difference can be seen in the ϵ_2 spectra where the 0.01 Ω cm sample shows definite structure at the crystalline silicon positions while the spectra of the 25 Ω cm samples are more featureless. In fact the ϵ_1 and ϵ_2 spectra of the high resistivity samples bear a striking resemblance to spectra calculated for amorphous SiO_2 ¹⁴, a 1:1 chemical mixture of silicon and oxygen. Detailed effective medium fits, required for quantitative analysis, are now in progress, but the shape of these spectra clearly favours a chemical mixture rather than a physical mixture¹¹. The spectra obtained here clearly indicate the better

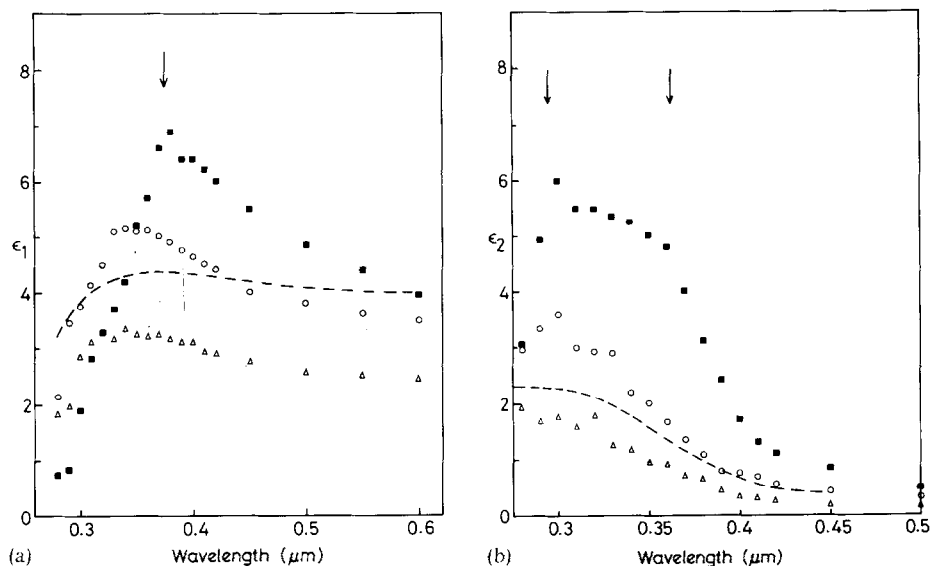


Fig. 5. (a) Real part ϵ_1 of the dielectric constant as a function of wavelength for high and low resistivity PS samples of various densities: ■, 0.01 Ω cm, 43%; ○, 25 Ω cm, 46%; △, 25 Ω cm, 36%. The spectrum of crystalline silicon⁶ shows a peak at the wavelength indicated by the arrow with a magnitude of about 43 (---, SiO spectrum¹⁴). (b) Imaginary part ϵ_2 of the dielectric constant as a function of wavelength for high and low resistivity PS samples of various densities: ■, 0.01 Ω cm, 43%; ○, 25 Ω cm, 46%; △, 25 Ω cm, 36%. The spectrum of crystalline silicon⁶ shows peaks at wavelengths indicated by the arrows with magnitudes of 35–45 (---, SiO spectrum¹⁴).

crystallinity of the low resistivity samples, a result consistent with the IR results discussed earlier.

Marked differences between high and low resistivity material are also observed in photoluminescence experiments, discussed in detail elsewhere¹⁰. An amorphous-like band is observed in high resistivity samples but not in 0.01 Ω cm samples. This band shifts in energy from about 1.47 to about 1.8 eV as the density is reduced, possibly as a result of increasing incorporation of oxygen and/or hydrogen, providing further evidence of chemical alloying.

4. CONCLUSIONS

The IR refractive index of PS was found to decrease as the density was reduced and an EMA was used to determine the density from the optical measurements. The method was shown to be a useful non-destructive technique for the measurement of density for low resistivity (0.01 Ω cm) samples, with good agreement with gravimetrically determined densities. Higher resistivity material (0.1–25 Ω cm), however, showed reduced values of n_{IR} , and hence apparently reduced densities, indicating the previously unsuspected result that partial oxidation had occurred on anodization. Thus higher apparent gravimetric densities than 45% will be required to produce dense oxidized PS in this material. The interference technique for the measurement of n_{IR} together with the gravimetric density assessment will therefore provide a useful

method for indicating the achievement of the optimum density for oxidation. The optical constants indicated that at high oxide concentrations the PS was of the form of a chemical mixture, SiO_x . All the techniques used in this study showed that $0.01 \Omega \text{ cm}$ samples had good crystallinity while higher resistivity samples of comparable density had poorer crystallinity.

ACKNOWLEDGMENT

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