Spectroscopic Ellipsometry Studies of Nanocrystalline Silicon in Thin-Film Silicon Dioxide

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ABSTRACT

Nanocrystalline silicon (n-Si) is formed in a silicon dioxide thin-film matrix by ion implantation followed by thermal annealing in forming gas at 1100 °C for 1 hour. The ion implantation is performed using multiple implants with different implantation energies and doses to create a quasi-flat concentration of silicon atoms throughout the silicon dioxide film. These samples are then analyzed using spectroscopic ellipsometry to characterize their linear optical properties. Implantations with small doses (5×10^{20} Si atoms/cm^3) increase the refractive index by a small amount (Δn~0.006 at 600nm), while implantations with moderate dose (5×10^{21} Si atoms/cm^3) have a larger increase in refractive index and exhibit optical absorption above ~1.9 eV (650 nm).

INTRODUCTION

There are many techniques for forming silicon nanocrystals with dimensions in the 3-10 nm range. One of the most intriguing utilizes ion implantation of silicon atoms into silicon dioxide followed by a high-temperature anneal to precipitate the excess silicon, resulting in embedded silicon nanocrystals.[1-4] These silicon nanocrystals have an intense, broad room-temperature photoluminescence (PL), peaking at 750-800 nm, with a full width at half-maximum of ~200 nm. Silicon nanocrystals can be formed either in bulk SiO_2 or in thin-film SiO_2 grown on a silicon wafer. Recently, there has been renewed interest in this material because several workers have shown evidence of optical gain.[1,2] Since SiO_2 is an essential material of the microelectronic industry, this discovery could have enormous economic impact in that it makes an all-silicon laser a distinct possibility.

In this paper, we discuss the spectroscopic ellipsometry results from a series of nanocrystalline silicon samples made in thin-film SiO_2. From these measurements, it is possible to determine film and interface thicknesses as well as spectroscopic refractive indices and extinction coefficients. This is particularly important for possible waveguide applications, where surface roughness, interface roughness, and small amounts of optical absorption are significant.

EXPERIMENTAL DETAILS

Sample preparation

Samples were prepared from oxidized silicon wafers fabricated using high-temperature wet oxidation, where the final oxide thicknesses were ~550 nm and ~1060 nm as determined by spectroscopic ellipsometry. These samples were ion-implanted using several different ion implantation energies and doses to create a quasi-constant concentration of silicon atoms throughout the film (see Fig. 1). As can be seen, the variation of concentration in the flat region is ~10% of the average concentration in the "flat" part of the spectrum. Since the maximum of the deepest implant peaks at the SiO_2-Si interface, there is considerable knock-on damage in the silicon layer just below the SiO_2 film. The samples are summarized in Table 1.

Table 1: Samples examined in this study

Sample	SiO_2 thickness (nm)	Si conc. ($x10^{20}$ Si/cm^3)
1	550	5
2	550	50
3	1060	50
4	550	200

Silicon nanoparticles were formed by annealing the samples at 1100 °C in a forming gas atmosphere (96% Ar, 4% H_2). This annealing step has been shown[3,4] to create a nearly uniform concentration of silicon nanoparticles with a concentration-dependent average diameter of 3-10 nm. This step removes most of the knock-on damage in the upper silicon layer, but some damage may remain in the heaviest implanted sample.

Photoluminescence (PL) measurements were made on these films, showing behavior that is consistent with previous spectra. The strongest PL was observed from samples 2 and 3, with a peak at 800 nm and a full width at half maximum of 160 nm. Sample 1 showed very little PL intensity, while sample 4 showed a much broader, lower intensity PL peak than samples 2 and 3, but still considerably more intense than sample 1.

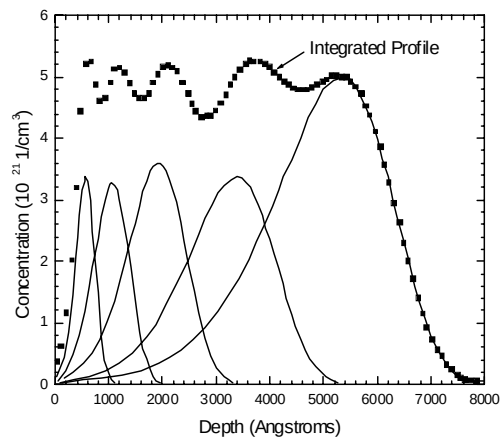

Figure 1. Concentration profile for 5 implants designed to give a quasi-flat profile throughout a 550 nm thick film. The 5 different energies used were 35, 70, 125, 210, and 325 keV, resulting in the integrated profile depicted by the square data points.

Spectroscopic ellipsometry and data analysis

Spectroscopic ellipsometry measurements were performed using the two-modulator generalized ellipsometer (2-MGE)[5] from 220 –850 nm (~1.46 to 5.64 eV). For isotropic samples, this instrument measures all the associated ellipsometry parameters:

$$N = \cos(2\psi); \quad S = \sin(2\psi)\sin(\Delta); \quad C = \sin(2\psi)\cos(\Delta), \qquad (1a,b,c)$$

where the angles ψ and Δ are the standard ellipsometry angles. The N, S, and C parameters are related to the standard ellipsometry parameters by

$$\rho = \frac{r_p}{r_s} = \tan\psi e^{i\Delta} = \frac{C + iS}{1 + N} \tag{2}$$

where r_p (r_s) are the complex reflection ratios for light polarized parallel (perpendicular) to the plane of incidence, respectively.

In order to determine useful parameters from spectroscopic ellipsometry data such as film thicknesses, interface and surface roughnesses, spectroscopic refractive indices and extinction coefficients, and optical band gaps, a model must be constructed and fit to the data.[6] Therefore, a critical part in any spectroscopic ellipsometry experiment is fitting the data to an appropriate model, and using a reasonable figure of merit function to determine whether or not the model fits the data within the error limits of the experiment. Typically, one uses the reduced χ^2 figure of merit, given by:

$$\chi^2 = \frac{1}{2N - m}\sum_{i=1}^{N}\left\{\left[\frac{\rho_{calc}^{real}(\lambda_i, \mathbf{z}) - \rho_{data}^{real}(\lambda_i)}{\delta\rho_{data}^{real}(\lambda_i)}\right]^2 + \left[\frac{\rho_{calc}^{imag}(\lambda_i, \mathbf{z}) - \rho_{data}^{imag}(\lambda_i)}{\delta\rho_{data}^{imag}(\lambda_i)}\right]^2\right\} \tag{3}$$

where N is the total number of points, λ_i is the wavelength of the ith point, m is the dimension of the vector of fitted parameters **z**, and $\delta\rho$ is the estimated error (including both random and systematic errors) of the ρ data. A good fit is then characterized by a χ^2 of ~1.

RESULTS AND DISCUSSION

Figure 2 shows spectroscopic ellipsometry data from the sample with the lowest implanted silicon density (Sample 1) as well as the fit to the data. The model consists of two layers: the n-Si SiO_2 layer modeled using a Sellmeier approximation,

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - \lambda_o^2}, \tag{4}$$

and an interface layer modeled using the Bruggeman effective medium approximation (EMA)[6] with 50% SiO_2 and 50% Si. The resulting fit was very good (χ^2 = 0.44), and showed that the n-Si+SiO_2 film had a marginally higher refractive index than the unimplanted SiO_2 film, resulting in A (SiO_2) = 1.096 and A (n-Si + SiO_2) = 1.108. (In terms of refractive indices at 600 nm, n(SiO_2) = 1.457 and n(n-Si + SiO_2) = 1.463.) The film thickness increased from 543.5 nm to 549.3 nm from the creation of the n-Si, and the interface layer increased from 0.8 to 1.8 nm.

Samples 2 and 3 had a concentration of 5 x 10^{21} Si atoms/cm^3 and produced the highest intensity PL. To fit the ellipsometry data from these samples (not shown), significantly more complicated models were employed. For the case of sample 2, the implant profile was similar to that shown in Fig. 1, although the concentration of silicon atoms was about a factor of 10 larger. Very little silicon is deposited in the top ~25 nm of the sample, and some significant amount of the silicon is deposited into the silicon substrate,

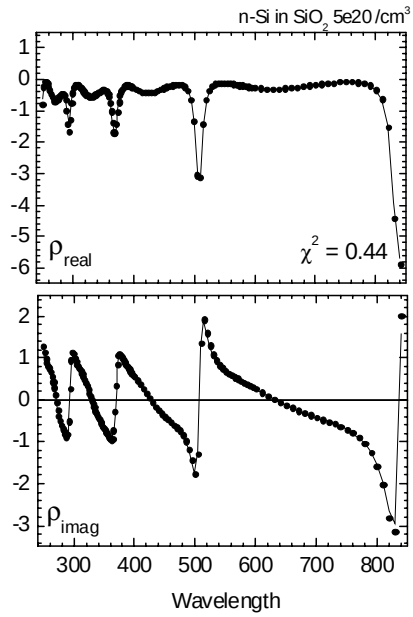

Figure 2: The real and imaginary parts of ρ of the 5 x 10^{20} Si atoms/cm^3 for an ellipsometry experiment taken at an angle of incidence of 65°.

since the SiO_2 film is ~550 nm thick. As a result, a reasonable model would consist of at least two layers: a surface layer, modeled using the optical functions of SiO_2, and the main layer consisting of a Maxwell-Garnett EMA,[8] where the main constituent is the SiO_2 matrix and a second component representing the n-Si inclusions. The optical functions of the n-Si inclusions are parameterized using the Tauc-Lorentz (T-L) model.[9] Altogether, seven parameters are fit to the data: the thickness of the top SiO_2 layer, the thickness of the main film, the fraction of n-Si, and four parameters of the T-L model. The results from the fit are shown in Table 2, and the spectroscopic refractive index and extinction coefficient determined from the fitting procedure are shown in Fig. 3 for the composite n-Si + SiO_2. The value of n is considerably higher than SiO_2, and there is no observable optical absorption below ~2 eV (~650 nm), indicating that this material may be a good candidate for optical waveguides for wavelengths greater than 650 nm.

As can be seen, the χ^2 is 0.60, meaning that the model does fit the data. Although the T-L model is primarily used to model amorphous materials, it is quite successful here. If one were to use the optical functions of fine-grain polycrystalline silicon, still varying the thicknesses and the fraction of p-Si in the SiO_2 matrix, the resulting χ^2 is 2.97, which is considerably worse than the fit using the T-L model. This indicates that the linear optical properties of the n-Si inclusions are closer to amorphous-like. Figure 4 shows the spectroscopic refractive index and extinction coefficient of various forms of silicon. Clearly, the refractive index of n-Si is considerably less than the other forms of silicon, and optical absorption occurs for photon energies greater than ~2eV.

Sample 3 started with a much thicker SiO_2 layer than did Sample 2 (see Table 1), The implantation doses were chosen so to give a similar silicon profile with the deepest penetration of silicon atoms ~900 nm; consequently, very little excess silicon was present in the bottom ~150 nm of the SiO_2 film. Furthermore, much higher energy implants were made. This required that the model used to interpret the spectroscopic ellipsometry data be more complicated than that employed for sample 2. Here, a 5-layer model was utilized. The first layer was a surface roughness layer, modeled using the Bruggeman EMA with

Table 2. Results of the fits to the ellipsometry data from samples 2 and 3. The quantity d is the thickness of the indicated layer.

Sample	2	3
Rough d (nm)	----	15±2
SiO_2 d (nm)	23.8±1.2	15±4
Film d (nm)	534.4±2.5	735±11
Graded d (nm)	----	175±16
SiO_2 d (nm)	----	94±14
n-Si Eg (eV)	2.02±0.2	2.03±0.02
f (n-Si)	0.12±0.02	0.09±0.01
n film at 600 nm	1.580	1.553
χ^2	0.60	2.37

50% voids, 50% n-Si+SiO_2, while the second layer was SiO_2, as with sample 2. The third layer was the film itself, again modeled using the Maxwell-Garnett EMA with a SiO_2 matrix and the n-Si inclusions, modeled using the T-L expressions. The third layer was a graded layer, where the optical properties varied linearly from the values of the main layer at the top to the optical properties of SiO_2 at the bottom. The 4th layer consisted of SiO_2. Altogether, 8 parameters were needed for this fit: the thicknesses of the 5 layers, the fraction of n-Si, and 2 of the 4 parameters of the T-L model. The results are summarized in Table 2.

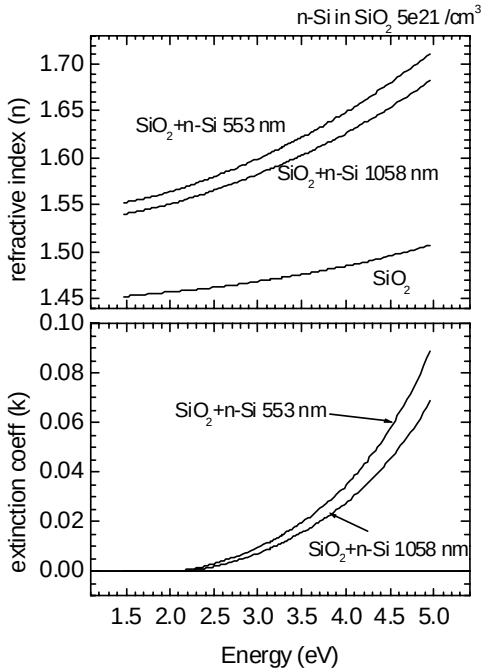

Figure 3. The refractive index and extinction coefficient for samples 2 and 3, and the refractive index of fused SiO_2.

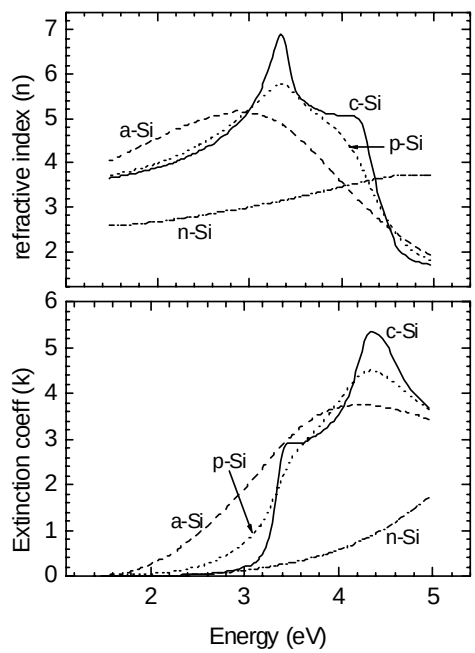

Figure 4. The optical functions for several different types of silicon determined from spectroscopic ellipsometry. a-Si = amorphous silicon (ref 10), p-Si = polycrystalline silicon (ref 10); c-Si = single crystal silicon (ref 11); n-Si = nanocrystalline silicon (this work).

As can be seen, the final value of the fitting figure of merit χ^2 is 2.37, indicating that the model does NOT fit the data (within its error limits). However this value is low enough to give some confidence that the selected model is close. Furthermore, the model used is just a logical extension of the model used for sample 2, where a very good fit is obtained. As can be seen from Fig. 3, the refractive index and extinction coefficients for the n-Si + SiO_2 layer are similar for the two samples.

The sample with the highest dose of n-Si is known to be a very complicated material, with larger nanocrystals and possibly connections between the nanocrystals. It is therefore not surprising that the ellipsometry data from this sample was even more difficult to fit, and only approximate estimates of the complex refractive index could be made, even with a more complicated model. Only when the fitting region is restricted to 515-870 nm, can a reasonable value of χ^2 be obtained ($\chi^2 = 0.62$); larger fitting regions result in considerably higher values of χ^2.

An examination of the ellipsometry data for Sample 4(not shown) does give some indication of the optical properties of the n-Si + SiO_2 layer. For wavelengths below ~320 nm, there is no evidence of oscillations in ρ, stating that light is not penetrating to the SiO_2/c-Si interface and the light penetration depth is considerably less than 1 micron. From ~320 to 500 nm, the oscillations increase in magnitude, indicating an increase of the light intensity at the SiO_2/c-Si interface and therefore a gradual decrease in optical absorption.

CONCLUSIONS

Spectroscopic ellipsometry measurements have been performed on four samples with nanocrystalline silicon particles imbedded in a thin-film SiO_2 matrix. Under the best circumstances, these measurements and the associated fits can determine film thickness, roughness thickness, and spectroscopic refractive index and extinction coefficient. Lightly implanted samples (~ 5×10^{20} Si atoms/cm^3) increase the refractive index slightly from that of undoped thin-film SiO_2. Moderately implanted samples (~ 5×10^{21} Si atoms/cm^3) result in significant optical absorption above ~2 eV (~650 nm), and a refractive index increase of ~0.1 at 600 nm). A very heavily implanted sample (~ 2×10^{22} Si atoms/cm^3) is complicated and no definitive statements can be made from the ellipsometry data.

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