Optical Properties of Silicon Nanocrystals Embedded in SiO_2 Matrix

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ABSTRACT

From the view point of both science and technology, it would be interesting and useful to examine the optical properties of isolated silicon nanocrystals (*nc*-Si) embedded in SiO_2 matrix. A good understanding to optical properties of the *nc*-Si is definitely important to both the quantum physics and the applications especially in optoelectronic and photonic devices. In this work, spectroscopic ellipsometry (SE), which is a nondestructive method, is employed to determine the optical properties including refractive index, extinction coefficient and absorption coefficient of the *nc*-Si with a mean size of ~ 4.2 nm embedded in a SiO_2 matrix in the photon-energy range of 1.13 - 4.96 eV (or wavelengths of 250 - 1100 nm). It is shown that the optical properties of the *nc*-Si are well described by the four-term F-B (Forouhi-Bloomer) model. A large band gap expansion (~ 0.6 eV) is observed for the *nc*-Si, indicating a significant quantum confinement effect. The bandgap expansion is in accordance with the firs-principle calculation of *nc*-Si optical bandgap based on quantum confinement.

Keywords: silicon nanocrystals (*nc*-Si), spectroscopic ellipsometry (SE), optical constants, dielectric functions, quantum confinement,

INTRODUCTION

Crystalline silicon nanoparticles or nanocrystals (*nc*-Si) embedded in a SiO_2 matrix have received considerable attention in recent years because of their promising applications in optoelectronic devices, memory devices and single electron devices with the main advantage of its full compatibility with silicon technology [1-6] . One promising method of forming silicon nanocrystals in a dielectric film relies on silicon ion implantation into SiO_2 and subsequent high temperature annealing [5-6]. Important advantages of this approach are the precise control for the *nc*-Si depth distribution and being able to form *nc*-Si of smaller size (~ 2 - ~ 5 nm) and a narrow size distribution of *nc*-Si. By this technique, these advantages can be easily achieved by adjusting ion implantation energy and dosage and the annealing conditions. There have been intensive studies on the light emitting mechanism of *nc*-Si formed by this technique, but very few experimental studies have focused on determining the optical properties of isolated Si nanocrystals embedded in SiO_2 matrix. In this study, we present an experimental study on optical properties of Si nanocrystals embedded in a SiO_2 matrix synthesized by this technique. Such a study is obviously important to the fundamental physics as it is concerned with a quantum system of quasiparticles with a size of less than ~ 5 nm isolated by a dielectric matrix, and it is also necessary to device applications especially in Si nanocrystals based optoelectronic and photonic devices.

There have been many reports focusing on the theoretical calculations of optical properties of semiconductor nanocrystals using various methods such as empirical-pseudopotential approach and *ab initio* technique in the recent years [7-9]. In contrast, very few experimental studies of optical properties of *nc*-Si have been reported. Especially, it is difficult to experimentally determine the optical properties of *nc*-Si embedded in a dielectric matrix, because the embedded Si nanocrystals can not be directly investigated by experiment. In our previous studies, we have reported the optical properties of *nc*-Si embedded in a SiO_2 matrix in the photon energy range of 1.1 - 3.1 eV [10, 11]. Nevertheless, there is still lack of a comprehensively experimental study of the optical properties in a wider photon energy range and a proper modeling to the optical properties. In this work, the optical properties including optical constants (refractive index and extinction coefficient), absorption coefficient of the *nc*-Si embedded in a SiO_2 matrix in the photon energy range of 1.13 - 4.96 eV have been determined with spectroscopy ellipsometry (SE). In our opinion, SE can give more complete and detailed information than that obtained from absorbance or reflectance measurements, because SE measurement takes into account polarization of light. The measured values, ellispsometric angles (Ψ and Δ), are related to the ratio of Fresnel reflection coefficients r_p and r_s through the equation $r_p / r_s = \tan(\Psi)\exp(\Delta)$. Dielectric function and optical constants (refractive index and extinction coefficient) can be extracted from the best fitting of Ψ and Δ. The optical constants are well modeled by the Forouhi-Bloomer formulism [12], and the modeling yields the energy bandgap of the *nc*-Si. A strong dielectric suppression and a large bandgap expansion are observed for the *nc*-Si.

EXPERIMENT

The sample under investigation was synthesized by Si^+ implantation with a dose of 1×10^{17} atoms/cm^2 at 100 keV into a 550-nm-thick SiO_2 film on *p*-type Si substrate followed by an annealing at 1000 ^{o}C for 30 minutes in nitrogen gas. The average size of *nc*-Si was determined from the broadening of the Bragg peak in XRD spectrum

NSTI-Nanotech 2005, www.nsti.org, ISBN 0-9767985-1-4 Vol. 2, 2005

by Scherer's equation

$$D = \frac{0.9\lambda}{\Delta\theta \cos(\theta_B)}, \quad (1)$$

where D is the mean diameter of nanocrystals, λ is the wavelength of the x-ray, θ_B is the Bragg angle and $\Delta\theta$ is the full width of the half maximum (FWHM) of the Bragg peak. Figure 1 shows the XRD measurement of *nc*-Si embedded in SiO_2 matrix and the pseudo-Voigt fit to the data, and the mean *nc*-Si size obtained is ~ 4.2 nm.

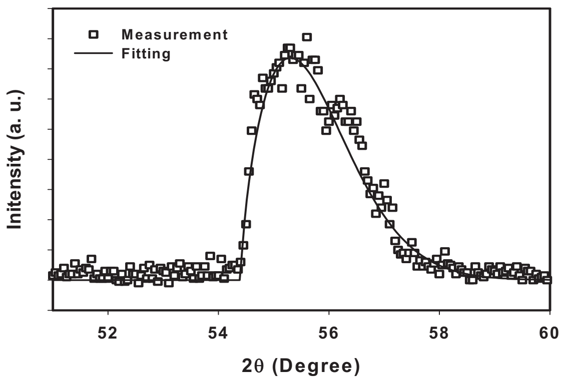

Figure 1: XRD measurement for the *nc*-Si embedded in a SiO_2 matrix and the pseudo-Voigt fit to the data.

In the SE analysis, the thin film system is represented by two layers, namely, the first layer (0≤depth≤250 nm) with *nc*-Si distributing in SiO_2, and the second layer (depth>250 nm) is just a pure SiO_2 layer without *nc*-Si. The *nc*-Si distribution in the SiO_2 thin film is determined from secondary ion mass spectroscopy (SIMS) measurement. Figure 2 shows the best-fit multi-layer model for the SiO_2 film containing silicon nanocrystals and the volume fraction of silicon nanocrystals in SiO_2 calculated from SIMS measurement.

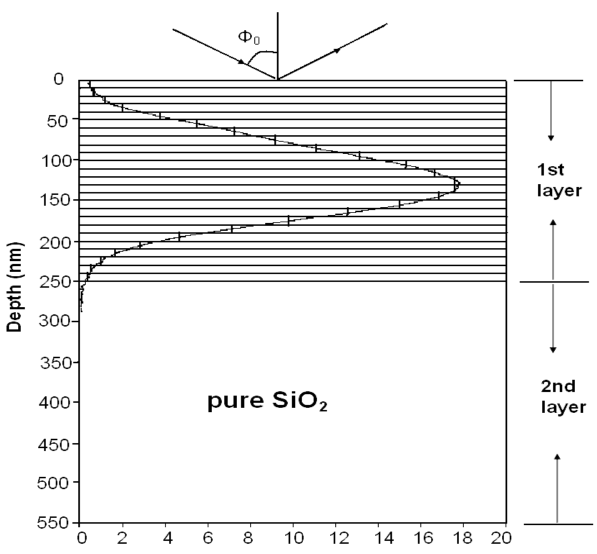

Figure 2: Multi-layer model used in the SE analysis. The *nc*-Si volume fraction is calculated from the SIMS measurement.

As shown in figure 2, in the first layer, the optical properties vary with the depth as the volume fraction of the *nc*-Si varies with depth. In order to model the optical properties of the first layer, it is then divided into 25 sub-layers with equal thickness d_0 = 10 nm. The volume fraction of *nc*-Si in each sub-layer is determined from SIMS measurement, and the *nc*-Si volume fraction is considered to be constant within each sub-layer. Each sub-layer has its own effective dielectric function ε_i (i = 1, 2,… 25) due to its own *nc*-Si volume fraction. Dielectric function of any medium can be described by optical constants through the following equation:

$$\varepsilon(E) = (n(E)^2 - k(E)^2) + i \bullet 2n(E)k(E). \quad (2)$$

As such, it can be optically schematized as an effective medium, in which the SiO_2 is the host matrix while the *nc*-Si is an inclusion embedded in the SiO_2 matrix, represented by the Maxwell-Garnett effective medium approximation (EMA)

$$\frac{\varepsilon_i - \varepsilon_{SiO_2}}{\varepsilon_i + 2\varepsilon_{SiO_2}} = \frac{\varepsilon_{nc-Si} - \varepsilon_{SiO_2}}{\varepsilon_{nc-Si} + 2\varepsilon_{SiO_2}} f_i, \quad (3)$$

where ε_i is the effective complex dielectric function of the i^{th} sub-layer, ε_{SiO_2} is the dielectric function of SiO_2 matrix, ε_{nc-Si} is the dielectric function of the *nc*-Si, and f_i is the volume fraction of *nc*-Si in the i^{th} sub-layer. As the volume fraction (f_i) and ε_{SiO_2} are known, from Eq. (3) the effective complex dielectric function ε_i (and thus the effective complex refractive index N_i) for the i^{th} sub-layer (i=1, 2, ...25) can be expressed in terms of ε_{nc-Si} (or the refractive index and extinction coefficient of *nc*-Si). Therefore, in the SE analysis, the ellipsometric angles (Ψ and Δ) can be expressed as functions of the optical constants of the *nc*-Si, although these functions cannot be displayed with analytical formulas due to their extreme complexity. To avoid solving such complicated equations, a SE spectra fitting is performed to determine the optical constants at each wavelength in the wavelength from 250 to 1100 nm.

In the SE spectra fitting, a proper optical dispersion model should be used to describe the spectra dependence of *nc*-Si optical constants. In this study, the four-term Forouhi-Bloomer (F-B) model is found to be the most suitable one to yield a reasonable fitting. In the four-term F-B model, Optical constants (refractive index n and extinction coefficient k) of silicon nanocrystals given by [12]:

$$k(E) = \left(\sum_{i=1}^{4} \frac{A_i}{E^2 - B_i E + C_i}\right)\left(E - E_g\right)^2, \quad (4)$$

$$n(E) = n(\infty) + \sum_{i=1}^{4} \frac{B_{0_i} E + C_{0_i}}{E^2 - B_i E + C_i}, \quad (5)$$

where

$$B_{0_i} = \frac{A_i}{Q_i}\left(-\frac{B_i^2}{2} + E_g B_i - E_g{}^2 + C_i\right), \quad (6)$$

$$C_{0_i} = \frac{A_i}{Q_i}\left((E_g^2 + C_i)\frac{B_i^2}{2} - 2E_g C_i \right), \quad (7)$$

$$Q_i = \frac{1}{2}(4C_i - B_i^{\,2})^{\frac{1}{2}}. \quad (8)$$

Fitting parameters of the model are A_i, B_i, C_i (i = 1, 2, 3, and 4), $n(\infty)$, and energy bandgap E_g. For an efficient fitting, the initial fitting parameters are taken equal to that of bulk crystalline silicon. Figure 3 shows the best spectra fitting, i.e., the comparison of the experimental ellipsometric angles (Ψ and Δ) with the calculated Ψ and Δ in the wavelength range from 250 to 1100 nm.

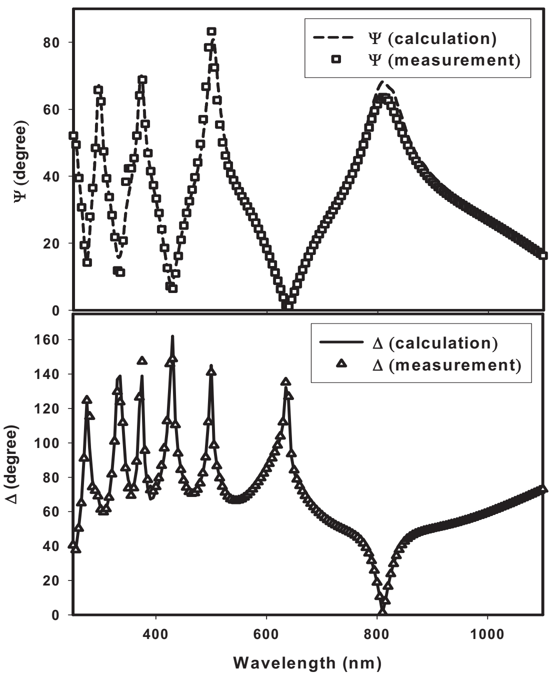

Figure 3: Best spectra fitting of ψ and Δ based on the F-B model with the approach described in the text.

As can be seen in this figure, all the complicated spectra features of both Ψ and Δ are fitted excellently, and the fitting yields reasonable values of all the parameters. This indicates that the above approach is correct, and the four-term F-B dispersion relations can describe the spectral dependence of the optical constants of the *nc*-Si accurately.

RESULTS AND DISCUTIONS

The fitting yields the parameters A_i, B_i, C_i (i = 1, 2, 3, and 4) and $n(\infty)$ of the F-B model and the energy bandgap (E_g) for *nc*-Si, which are shown and compared to their corresponding values of bulk crystalline silicon in table 1. The optical constants of the *nc*-Si are calculated with Eq. (4) and Eq. (5) using the parameters given by table 1. The optical constants of the *n*c-Si are shown in figure 4. The optical constants of bulk crystalline silicon are also included in the two figures for comparison. As can be seen in figure 4, the Si nanocrystals show a significant reduction in the optical constants and as compared to bulk crystalline silicon.

	A_i	B_i	C_i	$n(\infty)$	E_g
Bulk	0.0036	6.881	11.849	2.369	1.12
crystalline	0.014	7.401	13.747		
silicon	0.0683	8.634	18.795		
	0.0496	10.234	26.503		
Silicon	0.0538	7.112	12.718	2.824	1.737
nanocrystals	0.0056	8.016	16.080		
embedded	0.0603	8.030	18.710		
in SiO_2	0.0003	10.323	26.645		

Table 1: Values of the parameters A_i, B_i and C_i (i=1, 2,3,4), $n(\infty)$ and E_g of the F-B model for both bulk crystalline silicon and the *nc*-Si embedded in SiO_2.

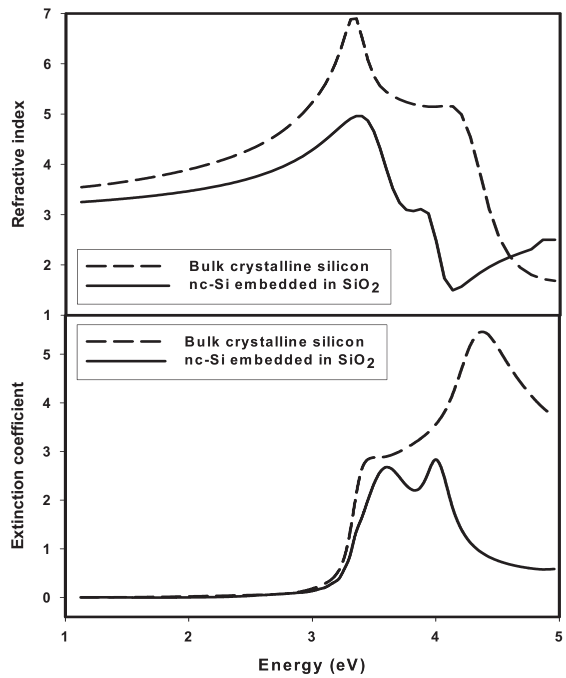

Figure 4: Refractive index (n) and extinction coefficient (k) of the *nc*-Si and bulk crystalline silicon as functions of wavelength.

It has been well known that reduction of the static dielectric constant becomes significant as the size of the quantum confined physical systems, such as quantum dots and wires, approaches the nano-metric range [13-15]. In our study, the static dielectric constant of the *nc*-Si embedded in SiO_2 matrix is 9.7, which is obtained from the calculation with the four-term F-B model by setting the photon energy to zero in Eq. (2). Taking into account the quantum confinement effect and screening effect, Wang *et al.* [7] pointed out that the static dielectric constant of the *nc*-Si as a function of the nanocrystal size could be expressed as follows:

$$\varepsilon_r(D) = 1 + \frac{\varepsilon_r(\infty) - 1}{1 + \left(\frac{6.9}{R} \right)^{1.37}} \quad (9)$$

where $\varepsilon_r(\infty)$ is the static dielectric constant of bulk crystalline silicon, and R is the radius of *nc*-Si with the unit of angstrom. Based on Eq. (9), where $\varepsilon_r(D)$ and $\varepsilon_r(\infty)$ are 9.7 and 11.4 respectively, the diameter of *nc*-Si is found to be ~ 4.5 nm, which is very close to the XRD result (the mean size is ~ 4.2 nm) mentioned above.

Although it is still uncertain that the reduction of dielectric constant is due to the opening of the bandgap, a bandgap expansion is indeed observed in this work for the *nc*-Si. As given in table 1, the bandgap of the *nc*-Si is 1.74 eV, which shows a bandgap expansion of ~ 0.6 eV as compared to the bandgap of bulk crystalline silicon. The bandgap obtained in this work is in very good agreement with the first-principle calculation of the optical gap of silicon nanocrystals in Ref. [16] based on quantum confinement. On the other hand, the size distribution of the *nc*-Si could be estimated from the energy bandgap expansion. Assuming a log-normal size distribution for the nc-Si, the size distribution could be calculated with the following equation proposed by Ranjan *et al.* [17]:

$$\Delta E_g = \frac{3.9}{{d_0}^n}\left(\frac{d_m}{d_0}\right)^{n[2n+5]/3}, \qquad (10)$$

where d_0 (in nm) is the mean size of nanocrystals, d_m is the size for which the maximum occurs in the log-normal distribution, and n = 1.22. For $\Delta E_g = 0.6$ eV and $d_0 = 4.2$ nm, the calculation with Eq. (11) yields $\frac{d_m}{d_0} = 0.96$. This indicates that the *nc*-Si has a very uniform size distribution, being consistent with the general belief that silicon nanocrystals synthesized by ion implantation have a narrow size distribution. A narrow size distribution is very useful to device applications of the *nc*-Si.

SUMMARY

In summary, we have developed a nondestructive approach to study the optical properties of silicon nanocrystals embedded in SiO_2 matrix by spectroscopic ellipsometry based on Maxwell-Garnett effective medium approximation. Thanks to the *nc*-Si depth profile obtained from SIMS measurements and a proper multi-layer model, we have done a complete optical characterization of silicon nanocrystals formed into SiO_2 film in a wide range of 1.13 - 4.96 eV. Optical constants and dielectric functions of *nc*-Si embedded in SiO_2 matrix have been obtained from the best spectra fitting based on the four-term F-B model. It is shown that there are a remarkable dielectric suppression and a large bandgap expansion due to the quantum size effect. The mean size of silicon nanocrystals obtained from the dielectric suppression is consistent with the result of XRD measurement. The bandgap of the *nc*-Si is ~ 1.7 eV, showing a large bandgap expansion of ~ 0.6 eV. The bandgap expansion is in very good agreement with the first-principle calculation of the optical gap of silicon nanocrystals based on quantum confinement effect.

This work has been financially supported by the Ministry of Education Singapore under project NO. ARC 1/04.

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