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<td>Ding, Liang; Chen, Tupei; Liu, Yang; Liu, Yu Chan</td>
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A comparative study on the dielectric functions of isolated Si nanocrystals and densely-stacked Si nanocrystal layer embedded in SiO2 synthesized with Si ion implantation

L. Ding*, a, T. P. Chen, a, Y. Liu, a and Y. C. Liu b

a School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798; b Singapore Institute of Manufacturing Technology, Singapore 638075

ABSTRACT

Both isolated Si nanocrystals (nc-Si) dispersedly distributed in a SiO2 matrix and densely stacked nc-Si layers embedded in SiO2 have been synthesized with the ion implantation technique followed by high temperature annealing. The dielectric functions of the isolated nc-Si and densely-stacked nc-Si layer embedded in SiO2 have been determined with spectroscopic ellipsometry (SE) in the photon energy range of 1.1-5 eV. The dielectric functions of these two different Si nanostructures were successfully extracted from the SE fitting based on a multi-layer fitting model that takes into account the distribution of nc-Si in SiO2 and a five phase model (i.e., air/SiO2 layer/densely-stacked nc-Si layer/SiO2 layer/Si), respectively. The dielectric spectra of isolated nc-Si distributed in SiO2 present a two-peak structure, while the dielectric spectra of densely-stacked nc-Si layer show a single broad peak, being similar to that of amorphous Si. The dielectric functions of these two Si nanostructures both show significant suppressions as compared with bulk crystalline Si. However, it has been observed that the densely stacked nc-Si layer exhibits a more significant suppression in the dielectric spectra than the isolated nc-Si dispersedly embedded in SiO2. This is probably related to the two factors: (i) the nc-Si size (~3 nm) of the densely stacked nc-Si layer is smaller than that (~4.5 nm) of the isolated nc-Si embedded in SiO2 matrix, and (ii) the densely stacked nc-Si layer has an amorphous phase.

Keywords: Si nanocrystals, implantation, dielectric function, ellipsometry

1. INTRODUCTION

There has been increasing research interest in Si nanostructures since the discovery of strong photoluminescence (PL) from porous Si.1 Si nanocrystals (nc-Si) embedded in a dielectric matrix have been extensively studied as they provide the possibility for applications in Si-based optoelectronic devices, memory devices, and single electron devices with the advantage of being compatible with the mainstream complimentary metal-oxide-semiconductor (CMOS) technology in the semiconductor industry. 1-5 Various techniques have been employed to synthesize nc-Si, including chemical vapor deposition (CVD),6-8 silicon ion implantation into SiO2,9,10 sputtering,11 and pulse laser deposition (PLD).12,13 Among all these techniques, silicon ion implantation into a SiO2 matrix followed by high temperature annealing is considered as one of the most promising methods for producing chemically and electrically stable nc-Si. It also allows for an accurate control of the depth distribution of nc-Si within the SiO2 film and yields a smaller size (~10 nm) and a narrow size distribution of the nc-Si. With this technique, both isolated nc-Si dispersedly distributed in a SiO2 matrix6,9 and densely stacked nc-Si layers embedded in SiO212-15 can be synthesized depending on the implantation recipe.

The optical properties of continuous thin film of nc-Si synthesized by pulse laser pyrolysis of silane have been determined with spectroscopic ellipsometry.16 However, there have been few studies that deal with the experimental determination of the optical properties of densely stacked nc-Si layer embedded in a dielectric matrix. The optical properties of the densely stacked nc-Si layer should be different from that of both isolated nc-Si and continuous film of nc-Si. In addition, a comparative study on the dielectric functions of dispersedly distributed nc-Si in SiO2 and densely stacked nc-Si layer is needed for a comprehensive understanding of the optical properties of nc-Si synthesized by ion implantation. Dispersely distributed Si nanocrystals can be formed in SiO2 matrix with a high dose of Si ions implanted at a high or medium energy.6,7 In practical applications, a high dose (typically in the range of ~10^{16}~10^{17} cm^{-2}) Si ion implantation at a very-low energy (~2 keV) into a thin SiO2 film can form a densely stacked nc-Si layer embedded in the SiO2 matrix.12-15 In this work, the dielectric functions of dispersedly Si nanocrystals and densely stacked nc-Si layer embedded in SiO2 have been determined with spectroscopic ellipsometry (SE).

*ding0008@ntu.edu.sg
2. EXPERIMENTS

The dispersedly distributed nc-Si embedded in a SiO₂ matrix was synthesized by Si⁺ implantation with a dose of 10¹⁷ atoms/cm² at the energy of 100 keV into a 550-nm-thick SiO₂ film thermally grown on a p-type Si substrate. A thermal annealing at 1000 °C for 30 min in nitrogen gas was carried out for the formation of Si nanocrystals dispersedly distributed in the SiO₂ film. The nc-Si distribution in the SiO₂ thin film can be determined from the secondary ion mass spectroscopy (SIMS) measurement. The SIMS intensity I(x) due to the excess silicon in the Si⁺-implanted region at a given depth (x) can be obtained by deducting the Si SIMS signal of the pure SiO₂ region from the measured total Si SIMS signal which is from both the excess Si and the SiO₂ at the depth. The amount of excess Si at depth x should be proportional to the intensity I(x). The volume fraction of nc-Si at the depth should be proportional to the amount of the excess Si at the depth. Thus, the volume fraction f(x) of the nc-Si embedded in SiO₂ at depth x can be expressed as

\[ f(x) = \frac{Q I(x)}{N_{Si} \int_0^{d_{\text{max}}} I(x) dx} \]

where Q is the dose of implanted Si ions in the unit of atoms/cm², d_max is the maximum depth in SiO₂ beyond which no excess Si can be detected, and N_{Si} is the Si density in the unit of atoms/cm³. In this study, Q is equal to 10¹⁷ atoms/cm² and N_{Si} is 5×10²² atoms/cm³. Figure 1(a) shows the high resolution transmission electron microscopy (HRTEM) image of the nc-Si with an average diameter of ~4.5 nm dispersedly embedded in the SiO₂ matrix. Densely-stacked nc-Si layer were synthesized as follows. 30-nm SiO₂ thin films were thermally grown in dry oxygen at 950 °C on p-type (100) wafers. Si ions with a dose of 8×10¹⁶ cm⁻² were then implanted into the SiO₂ thin films at the energy of 1 keV. Postimplantation thermal annealing was carried out in the N₂ ambient at 1000 °C for 30 min. A densely stacked nc-Si layer with the thickness of ~16 nm embedded in SiO₂ is observed from the cross-sectional transmission (TEM) image, as shown in Fig. 1(b). The mean size of nc-Si is ~3 nm as determined from full width at half-maximum (FWHM) of the Bragg peak in the X-ray diffraction (XRD) measurements. Spectroscopic ellipsometry (SE) measurements were carried out in the wavelength range of 250-1100 nm with a step of 5 nm at the incident angle of 75° to determine the dielectric functions of the densely stacked nc-Si layer.

3. METHODOLOGY

The implanted Si distributes from the surface to the depth of ~250 nm, and the subsequent annealing does not change the profile significantly because of the extremely low diffusion coefficient of Si in SiO₂ films. There is almost no nc-Si beyond the depth of 250 nm in the SiO₂ film. In order to extract the dielectric functions of nc-Si embedded in SiO₂, the multilayer optical model shown in Fig. 2(a) was used to analyze the SE data. As can be seen in Fig. 2(a), the layer containing nc-Si, whose thickness d₁ is 250 nm, is divided into 25 sublayers with equal thickness d₀=10 nm. Each

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**Fig. 1.** (a) TEM image of dispersedly distributed nc-Si embedded in SiO₂; (b) TEM image of the densely-stacked nc-Si layer embedded in SiO₂.
sublayer can be optically schematized as an effective medium represented by the Maxwell-Garnett effective medium approximation (EMA). The Maxwell-Garnett EMA is characterized by the volume fraction of nc-Si which can be obtained from the SIMS measurement, the known dielectric functions of SiO₂, and the nc-Si dielectric functions that are to be determined. Therefore, the Maxwell-Garnett EMA can be used to extract the nc-Si dielectric functions from the SE spectral fitting. For the spectral fitting an optical dispersion model for the nc-Si is required. We have found that the four-term FB model is the suitable one that can yield a successful fitting. As such, the Maxwell-Garnett EMA based on the four-term FB model is used in the SE spectral fitting. In the spectral fitting, the optimization is carried out by freely varying the 14 parameters, which include the parameters \( A_i, B_i, C_i \) (\( i = 1, 2, 3, \) and \( 4 \)) for the four terms, the refractive index (\( n \)) when photon energy \( E \to \infty \), and the band gap \( E_g \) to minimize the mean-square error (MSE) (Ref. 18).

In the initial SE analysis for the samples with densely-stacked nc-Si layer embedded in SiO₂, we also tried to employ the multilayer model to fit the SE spectra, but no reasonable fittings could be achieved. This indicates that the multi-layer model is inadequate for the densely-stacked nc-Si layer synthesized with a high-dose (5×10¹⁶ cm⁻²) at very-low energy (1 keV). Therefore, a new model is required for the present study. In this study, as a densely stacked nc-Si layer is formed in the SiO₂ thin film, this nc-Si layer should be treated as one phase in the SE analysis. Therefore, in the SE analysis, the material system of the present study can be described by the five-phase model (i.e., air/SiO₂ layer/densely stacked nc-Si layer/SiO₂ layer/Si substrate), as shown in Fig. 2(b). In the fitting, the ellipsometric angles (Ψ and Δ) which are functions of both the film thickness and the optical constants of all the layers were fitted at each wavelength, thus no optical dispersion equation was required with the five-phase model.

Based on the methods mentioned above, excellent spectral SE fitting were achieved for both the dispersedly distributed nc-Si and densely-stacked nc-Si layer. Figure 3 shows the best spectral fittings for the dispersedly distributed nc-Si and densely-stacked nc-Si layer embedded in SiO₂ films. As can be seen in this figure, all the complicated spectral features of both Ψ and Δ can be fitted excellently, indicating that the models shown in Fig. 2 are effective. Figure 3 shows the dielectric functions of the dispersedly distributed nc-Si and densely-stacked nc-Si layer obtained from the fitting shown in Fig. 2(b). For comparison, the dielectric functions of other Si materials including the continuous nc-Si thin film deposited by pulsed laser pyrolysis of silane (Ref. 16), amorphous Si (Ref. 19) and bulk crystalline Si (Ref. 20) are also included in Fig. 3. As can be seen in Figs. 4, the overall spectral features of dielectric functions of nc-Si are similar to that of bulk crystalline Si. However, the nc-Si shows a significant reduction in the optical constants and dielectric function as compared with bulk crystalline Si. It has been well established 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 nanometric range.21,22 However, the origin of the reduction in the static dielectric constant with the size is still not fully understood. It is often attributed to the opening of the gap, which should lower the polarizability, but it is also

4. RESULTS AND DISCUSSIONS

Based on the methods mentioned above, excellent spectral SE fitting were achieved for both the dispersedly distributed nc-Si and densely-stacked nc-Si layer. Figure 3 shows the best spectral fittings for the dispersedly distributed nc-Si and densely-stacked nc-Si layer embedded in SiO₂ films. As can be seen in this figure, all the complicated spectral features of both Ψ and Δ can be fitted excellently, indicating that the models shown in Fig. 2 are effective. Figure 3 shows the dielectric functions of the dispersedly distributed nc-Si and densely-stacked nc-Si layer obtained from the fitting shown in Fig. 2(b). For comparison, the dielectric functions of other Si materials including the continuous nc-Si thin film deposited by pulsed laser pyrolysis of silane (Ref. 16), amorphous Si (Ref. 19) and bulk crystalline Si (Ref. 20) are also included in Fig. 3. As can be seen in Figs. 4, the overall spectral features of dielectric functions of nc-Si are similar to that of bulk crystalline Si. However, the nc-Si shows a significant reduction in the optical constants and dielectric function as compared with bulk crystalline Si. It has been well established 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 nanometric range.21,22 However, the origin of the reduction in the static dielectric constant with the size is still not fully understood. It is often attributed to the opening of the gap, which should lower the polarizability, but it is also

Fig. 2. (a) Multilayer model in the extraction of dielectric functions of dispersedly distributed nc-Si embedded in SiO₂; (b) Five-phase model used in the SE analysis for the determination of densely-stacked nc-Si layer embedded in SiO₂.

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shown that the reduction is due to the breaking of polarizable bonds at the surface and is not due to the opening of the band gap induced by the confinement. As can be seen in the figure, the dielectric spectra of the densely-stacked silicon nanocrystal layer are similar to that of amorphous Si but different from those of both bulk crystalline Si and the isolated nc-Si. For the imaginary part of dielectric functions, the densely-stacked silicon nanocrystal layer and amorphous Si show a single broadened peak; in contrast, bulk crystalline Si and the isolated nc-Si exhibit a two-peak structure. The peak structures in the spectra of the imaginary part of dielectric functions are believed to originate from singularities in the joint density of states (DOS). Essentially, the DOS in the amorphous state is a broadened version of crystalline state, which leads to a single broad peak in the dielectric spectra of amorphous semiconductors. Therefore, the single broadened peak observed for the densely-stacked silicon nanocrystal layer may suggest that the nanocrystal layer is in an amorphous state to certain extent. On the other hand, the nanocrystal layer also shows significant dielectric suppressions (i.e., reductions in the dielectric functions) as compared with bulk crystalline silicon and amorphous silicon, which is believed to be related to the size effect of the nanocrystals. Furthermore, it is observed that the dielectric functions of the densely-stacked nc-Si layer are suppressed much more than those of isolated nc-Si embedded in SiO₂. This is mostly related to: (i) the smaller size of nanocrystals (~3 nm) than that of isolated nc-Si, and (ii) the remaining amorphous phase of Si nanoclusters for the sample in this study. Therefore, we propose that the suppression of the dielectric spectra of the densely-stacked Si nanocrystal layer originates from both the quantum confinement effect and the remaining amorphous phase of the nc-Si layer, which also contributes to the single-peak structure of the dielectric spectra.

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**Fig. 3.** (a) Best spectral fitting for the sample with dispersedly distributed nc-Si in SiO₂; (b) Best spectra fitting for the sample with densely-stacked nc-Si layer embedded in SiO₂.

**Fig. 4.** (a) Real and imaginary parts of the complex dielectric functions of isolated nc-Si dispersedly distributed in a SiO₂ matrix, the densely-stacked Si nanocrystal layer. For comparison, the dielectric functions of the continuous nc-Si thin film (Ref. 14), amorphous Si (Ref. 16) and bulk crystalline Si (Ref. 17) are also included for comparison.
5. SUMMARY

In summary, isolated Si nanocrystals (nc-Si) dispersedly distributed in a SiO2 matrix and densely stacked nc-Si layers embedded in nc-Si layers have been synthesized with Si ion implantation and subsequent annealing. Dielectric functions of the two different nc-Si structures have been obtained in the photon energy range of 1.1-5.0 eV using SE analysis. The optical properties of the nc-Si dispersedly distributed in SiO2 are found to be well described by the four-term Forouhi-Bloomer model. The dielectric spectra of the nc-Si dispersedly distributed in SiO2 are similar to that of the bulk crystalline Si, although it shows a significant reduction as compared with bulk crystalline Si. The dielectric functions of the densely-stacked nc-Si layer embedded in SiO2 synthesized by low-energy Si+ implantation are suppressed much more than that of nc-Si dispersedly distributed embedded in SiO2 formed by high-energy Si+ implantation. It could be due to both the quantum confinement effect and the remaining amorphous phase of the densely-stacked nc-Si layer. The partially amorphous phase of the densely-stacked nc-Si layer also makes contributions to the single-peak structure of the dielectric spectra.

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REFERENCES


