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Characterization of Si nanorods by spectroscopic ellipsometry with efficient theoretical modeling

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Spectroscopic ellipsometry (SE) is applied to characterize Si columnar nanostructures. By employing effective medium approximation (EMA) theory, Si nanorods are treated as a graded layer with each sub-layer modeled as a mixture of Si and voids with varying porosity fraction. In addition, the rigorous coupled-wave analysis and finite-element Green's function method were used in modeling Si nanorods as a stack of disks with varying diameters and thicknesses, and the calculations are in satisfactory agreement with the measurement results.

1 Introduction Among various kinds of nanostructures which have been widely used in solar energy conversion, nanorods are very attractive because they naturally provide a directed path for electrical transport [1, 2]. In particular, Si nanorods are considered one of potential candidates for future solar cells because they can efficiently absorb light along the length of rods and collect the generated electricity [3]. Thus, fully understanding nanorods' structures and corresponding optical properties become an urgent issue. Conventionally, micro- and/or nanostructures are characterized using different types of microscopies, such as scanning electron microscopy, transmission electron microscopy, atomic force microscopy, etc. However, these microscopies either require additional sample preparations, or exert energetic electron beams or mechanical forces on samples, which inevitably produce irreversible damages. In contrast, spectroscopic ellipsometry (SE) is a non-contact and nondestructive optical technique for the characterization of thin films and bulk materials [4]. Its applications have extended from measuring optical constants and thicknesses toward more sophisticated characterizations such as electronic structures, chemical compositions, and micro-/nanostructures [5–7].

In this paper we report the application of variable-angle spectroscopic ellipsometry (VASE) to characterize Si nanorods. The Bruggeman effective medium approximation (EMA) [8] theory is employed in the analysis to model porous columnar structures. Moreover, we explore the capability of describing the nanorods' geometry and structures with the rigorous coupled-wave analysis (RCWA) [9, 10] as well as an efficient finite-element Green's function approach [11].

2 Experimental

2.1 Sample preparation The Si nanorods under investigation were fabricated by a Ni/SiO_2 nano-mask assisted dry-etching procedure. A 5 nm thick Ni film was first e-beam evaporated on the SiO_2/Si substrate, where the SiO_2 buffer layer (20 nm in thickness) was deposited by using plasma-enhanced chemical vapor deposition. Subsequently, a rapid thermal annealing process at 850 °C was performed to self-aggregate the Ni nano-dots on the

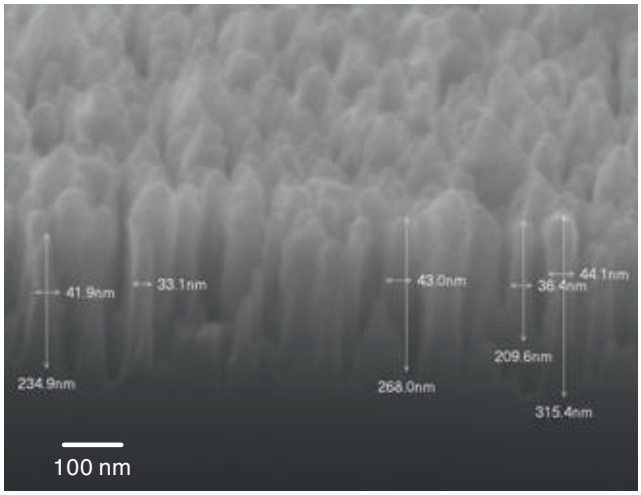

Figure 1 Scanning electron micrograph of Si nanorods.

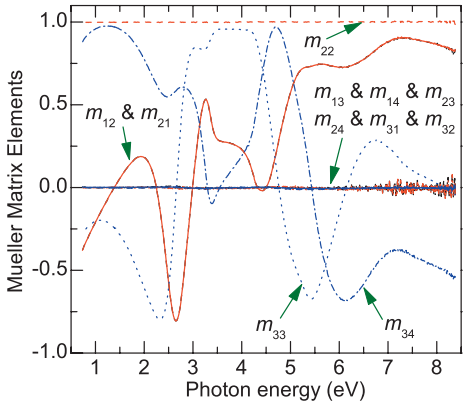

Figure 2 (online colour at: www.pss-a.com) Mueller-matrix measurements of Si nanorods at an incidence angle of 60°.

SiO_2/Si substrate. By using the Ni nano-dots as a nano-mask, the sample was dry-etched in a planar-type ICP-RIE system. The SiO_2 layer was then removed from the surface together with Ni nano-dots, leaving only Si nanorods standing on the Si substrate. The nanorods samples were stored in methanol to avoid gradual oxidation, and were dried with N_2 purge prior to measurements. Figure 1 displays one typical SEM image of the Si nanorods samples. As depicted in the figure, the diameter and height of nanorods are around 30–45 nm and 200–315 nm, respectively.

2.2 Variable-angle spectroscopic ellipsometry

The interaction of polarized light with a sample can be represented by the Jones matrix formalism [12, 13]:

$$\begin{bmatrix} E_p^{out} \\ E_s^{out} \end{bmatrix} = \begin{bmatrix} \tilde{R}_{pp} & \tilde{R}_{sp} \\ \tilde{R}_{ps} & \tilde{R}_{ss} \end{bmatrix} \cdot \begin{bmatrix} E_p^{in} \\ E_s^{in} \end{bmatrix}, \quad (1)$$

where $\tilde{R}_{pp}$ and $\tilde{R}_{ss}$ are complex Fresnel reflection coefficients of the sample for p- and s-polarized light, respectively. The off-diagonal terms $\tilde{R}_{ps}$ and $\tilde{R}_{sp}$ describe the cross-coupling of the p- and s-polarized light and are zero for an isotropic sample. Thus, ellipsometric measurements are normally described by two parameters Ψ and Δ in the following form:

$$\tan(\Psi) \cdot e^{i\Delta} = \frac{\tilde{R}_{pp}}{\tilde{R}_{ss}} . \quad (2)$$

Because of the charge screening effect developed by the columnar structure, as shown in Fig. 1, it can be expected that the Si nanorods may introduce anisotropy. Moreover, if the rods are inclined with respect to the sample surface, there may also be cross-polarization [7].

To characterize such a sample, we began with a Mueller-matrix measurement to test if there exist significant cross-polarization and depolarization for the Si nanorods. The SE data were acquired over a broad range from near infrared to vacuum ultraviolet (VUV) using a rotating-analyzer ellipsometer (RAE) system with an adjustable retarder (VUV-VASE, J. A. Woollam Co.), which can measure up to 11 Mueller-matrix elements (normalized to m_{11}) except the fourth row [12]. Since the m_{22} elements measured at several incident angles were close to unity, the sample could be regarded as non-depolarizing. Besides, the off-diagonal blocks of the Mueller-matrix elements (m_{13}, m_{14}, m_{23}, m_{24}, m_{31}, m_{32}) were basically zero to within the standard deviations of the measurement, as shown in Fig. 2. In terms of generalized ellipsometry, the off-diagonal ellipsometric ratios $\tilde{R}_{ps}/\tilde{R}_{pp}$ and $\tilde{R}_{sp}/\tilde{R}_{ss}$ were found to be almost zero as well. This suggests the Si nanorods can be treated as vertically standing columns on the substrate surface, and it is possible for us only to do normal ellipsometry measurement, which is sufficient for uniaxial anisotropy with the optical axis perpendicular to the surface.

3 Results and discussion

3.1 Analysis employing effective medium approximation In order to extract structural parameters of the Si nanorods, a physical model was established employing effective medium theory, which is developed to explain the connection between the microstructure of a heterogeneous thin film and the macroscopic dielectric responses [8]. Si nanorods can be considered as a thin film composed of comparable amount of crystalline Si and void, thus is suitable for the Bruggeman EMA. The optical constants of crystalline Si analyzed in Johs et al. [12] were used in the model.

Moreover, due to the anisotropic nature of columnar structures, charge screening factors must also be taken into consideration. Because different shapes of microstructures will induce distinct boundary conditions to the electrical and magnetic field in the medium, the depolarization factor q can be used to model the screening effect in an EMA mixture. For the Si nanorods, which are almost perpendicular to the surface (along z-direction), q_z must be close to 0 to model the vertical boundaries of nanorods, and the

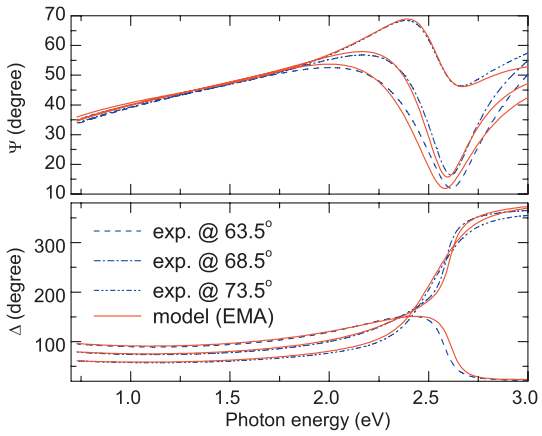

Figure 3 (online colour at: www.pss-a.com) Measurement results and model fits based on the graded, uniaxial EMA theory.

splitting between the other two components ($q_x = q_y \approx 1/2$) can describe the in-plane symmetry [5].

It was found that applying only the above two considerations would not give us reasonable results. As the SEM image displays (Fig. 1), the diameter of nanorods is by no means uniform along the vertical direction. Therefore, the Si nanorods were treated as a graded layer, in which each sub-layer is modeled as a mixture of crystalline Si and voids with varying porosity fraction. The uniaxial anisotropy of the nanorods was described by modeling the directional-dependence of the EMA screening factor. Figures 3 and 4 show the model fitting based on a 3-node, graded EMA layer and the corresponding depth profile of dielectric constants for nanorods, respectively. As expected, this model fit works well at longer wavelengths, where the EMA theory still holds for the feature sizes of the Si nanorods.

3.2 Analysis based on rigorous coupled-wave analysis and Green's function method Because the EMA theory only works well when the finite-wavelength effects are negligible [8], alternative modeling approaches are required in the SE analysis of nanostructures from short wavelengths comparable to the critical dimension of samples. Here, we explore the capability of modeling the Si

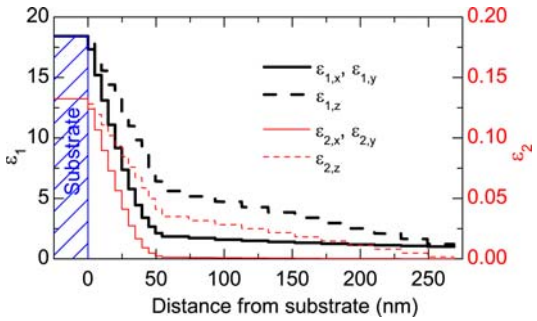

Figure 4 (online colour at: www.pss-a.com) Depth profile of anisotropic dielectric constants ε_1 (real part) and ε_2 (imaginary part) for Si nanorods at 2.48 eV.

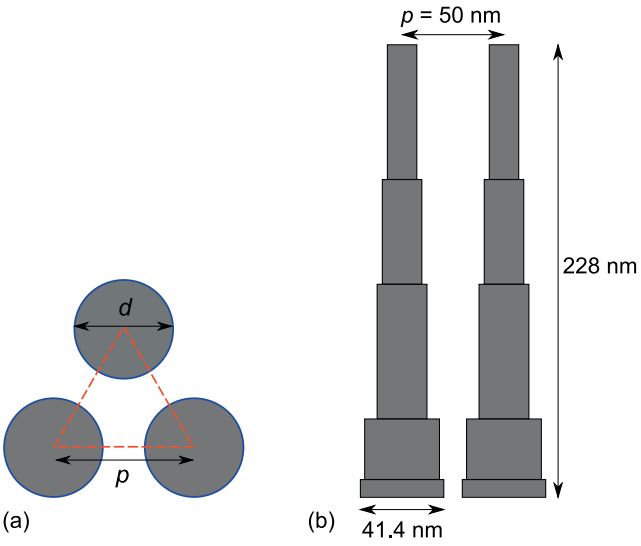

Figure 5 (online colour at: www.pss-a.com) (a) Triangular unit cell used in RCWA and GF calculations; (b) the cross-sectional view of the rods model with 5 cylinders.

nanorods using techniques conventionally applied only for periodic structures.

The RCWA may be the most popular method for the accurate diffraction analysis of periodic structures [9, 10], but it becomes terribly inefficient when applied to three-dimensional gratings. Hence, an efficient numerical method based on the Green's function (GF) approach [11] was employed as well in the modeling. Since the nanorods are very closely packed (Fig. 1), the unit cell for the RCWA and GF modelings was chosen to be a regular triangle, as shown in Fig. 5(a), which is the most tightly packed periodic structure in two dimensions.

To describe the structure, we started with partitioning the rods into a stack of 5 to 7 lamellar cylinders with different diameters and thicknesses. The unit vector length or the pitch p in a triangle unit cell was fixed at 50 nm at this stage because the same diameter-to-pitch ratio but different

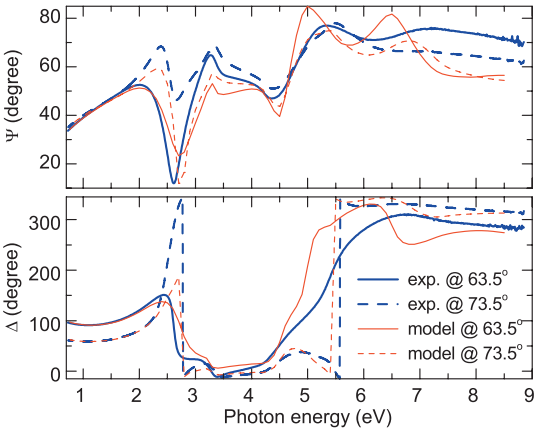

Figure 6 (online colour at: www.pss-a.com) SE measurement and model calculations of Si nanorods based on the GF method with a rod model shown in Fig. 5(b).

sets of values lead to very similar results. The diameter and thickness of each slice were first converted from the EMA result and then adjusted manually to find a better fit.

It is found that the RCWA and finite-element GF method give almost the same results, but calculations based on the GF approach are about one order of magnitude faster. Figure 5(b) illustrates the best nanorod geometry we found till now, and the comparisons between SE measurements and the GF approach calculations are depicted in Fig. 6. Although the simulated spectra do not match exactly with experimental data, the shapes are similar and trends are in good agreement.

3.3 Discussion The SE studies of columnar Si nanostructures from VUV to near-IR spectrum show that this technique could provide useful information about nanostructures, such as the effective dielectric constants or the geometric structure. The information found from the SE analyses not only agrees with what SEM micrograph revealed qualitatively but also quantitatively to a certain degree. The above analyses could be further improved by increasing the number of stacks and further fine-tuning the porosity fraction (when using EMA theory) or their thicknesses and diameters (when using the other two approaches). However, the more the stacks and/or other refinement employed, it is more likely that severe parameter correlation becomes unavoidable and an unique model could not be determined.

It should be noted that either the RCWA or GF approach has been applied only for periodic structures in the past. But the above model calculations (periodic) indicate that they could also be applied as an approximation for this kind of non-periodic nanostructures with good success.

4 Conclusion Fabrication of micro- and/or nanostructures requires accurate and reliable methods to characterize the processed structures such that their physical properties as well as fabrication quality can be controlled. Here we explore the capability of SE as a noninvasive characterization tool for columnar nanostructures. By applying EMA in the model fittings, the Si nanorods were found to present porosity variation along the vertical direction. The SE measurement and model-generated results can reach good agreement when introducing grading by dividing the nanorod layer into several sub-layers with varying thicknesses and void fractions. To overcome the EMA's inherent limitation due to the finite-wavelength effects, we employed the RCWA and an efficient GF method as alternative approaches to analyze SE measurements of Si nanorods. These modelings give reasonable fittings, and also support the results obtained from the EMA analysis. These findings demonstrate that SE could be a useful technique for the characterization of various kinds of structures in nano scale.

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References

[1] W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, Science **295**, 2425 (2002).
[2] B. R. Mehta and F. E. Kruis, Sol. Energy Mater. Sol. Cells **85**, 107 (2005).
[3] B. M. Kayes, H. A. Atwater, and N. S. Lewis, J. Appl. Phys. **97**, 114302 (2005).
[4] J. N. Hilfiker, C. L. Bungay, R. A. Synowicki, T. E. Tiwald, C. M. Herzinger, B. Johs, G. K. Pribil, and J. A. Woollam, J. Vac. Sci. Technol. A **21**, 1103 (2003).
[5] K. Kaminska, A. Amassian, L. Martinu, and K. Robbie, J. Appl. Phys. **97**, 013511 (2005).
[6] B. Kaplan, T. Novikova, A. D. Martino, and B. Drévillon, Appl. Opt. **43**, 1233 (2004).
[7] G. Beydaghyan, C. Buzea, Y. Cui, C. Elliott, and K. Robbie, Appl. Phys. Lett. **87**, 153103 (2005).
[8] D. E. Aspnes, Thin Solid Films **89**, 249 (1982).
[9] M. G. Moharam and T. K. Gaylord, J. Opt. Soc. Am. **71**, 811 (1981).
[10] M. G. Moharam, E. B. Grann, D. A. Pommet, and T. K. Gaylord, J. Opt. Soc. Am. A **12**, 1068 (1995).
[11] Y. C. Chang, G. Li, H. Chu, and J. Opsal, J. Opt. Soc. Am. A **23**, 638 (2006).
[12] B. Johs, J. A. Woollam, C. M. Herzinger, J. N. Hilfiker, R. Synowicki, and C. L. Bungay, Proceedings Optical Metrology, Denver, Colorado, USA (SPIE, Bellingham, 2000), pp. 29–58.
[13] M. Schubert, Ann. Phys. **15**, 480 (2006).