Reflectance of Sub-Wavelength Structure on Silicon Nitride for Solar Cell Application

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***Abstract*—In this study, reflection properties of sub-wavelength structures (SWS) on silicon nitride (Si_3N_4) antireflective coatings are investigated. Numerical calculation of SWS reflection based on a rigorous coupled-wave approach is conducted and compared with the measurement of fabricated samples. We compare the results of single- and double-layer-antireflection (SLAR and DLAR) coatings with SWS on Si_3N_4, taking into account average residual reflectivity over a range of wavelengths, where the solar efficiency is further estimated. A low average residual reflectivity of 9.56% could be obtained for a Si_3N_4 SWS height and non-etched layer of 140 nm and 60 nm respectively, which will be less than 80 nm Si3N4 SLAR (~15%) and almost the same as that of a DLAR with 60 nm Si_3N_4 and 70 nm magnesium fluoride (~10%).**

Keywords- Silicon Nitride; Sub-Wavelength Structure; Antireflection Coating, Reflectance, Efficiency, Maxwell Equations, Rigorous Coupled-Wave Approach, Modeling and Simulation, Fabrication and Characterization.

I. INTRODUCTION

The antireflection coating is a key factor for solar cells' design [1-3]. Many studies have been reported for double-layer-antireflection (DLAR) coatings because single-layer-antireflection (SLAR) coatings are not able to cover a broad range of the solar spectrum. Unfortunately, these multilayer antireflection coatings (ARCs) are expensive to fabricate owing to the stringent requirement of high vacuum, material selection, and layer thickness control. A well-known way to multilayer ARCs is the sub-wavelength structures (SWS) surface with dimensions smaller than the wavelength of light. To date, a wide variety of techniques was examined for texturing mc-Si cells [4]. One of the promising options is surface texturing by dry etching technique. Fabricating uniform textures with a submicron scale on mc-Si wafers by reactive ion etching (RIE) for Si solar cells [5-6], but experimental and theoretical studies on texturization of Si_3N_4 and its optical properties for solar cells' application has not been clearly drawn yet.

In this study, we fabricate sub-wavelength structures on ARC layers instead of semiconductor layer. The main motivation behind this lies in the fact that the sub-wavelength structures will act as a second ARC layer with an effective refractive index so that the total structure can perform as a DLAR layer with textured surface. We can cost down the deposition of the 2nd ARCs layer. Consequently, this technique can be saved with better or comparable performance as that of a DLAR solar cell. The reflectance data of the explored samples is calculated using a simulation of rigorous coupled-wave approach (RCWA). The optimized sub-wavelength structure is thus used to estimate the electrical data and efficiency.

II. SAMPLE FABRICATION AND NUMERICAL CALCULATION

A. *Experiment*

In this work, the sub-wavelength structure on silicon nitride ARCs of different heights are fabricated by a relatively simple method by using self assembled gold nano-masks and reactive ion etching (RIE) process [7]. First of all the polished (100) silicon was cleaned with dilute HF to remove the native oxide. For the fabrication process, first a layer of 200 nm thick silicon nitride (Si_3N_4) was first deposited on a polished (100) silicon wafer. A gold film with a thickness of 1.5 nm was then evaporated on the silicon nitride surface using an E-beam evaporating system. The gold film was then rapid thermal annealed (RTA) under the forming gas (mixture of H_2 and $N_{2)}$ with a flow rate of 3 sccm at 900^oC for 30 seconds to form gold clusters, which served as the etch masks for silicon nitride. The sample is then etched by reactive ion etching (RIE) to form the sub-wavelength structures by a gas mixture of CF_4/O_2 with flow rate of 400 sccm and 100 sccm respectively. The RF power and pressure were 100 w and 50 mTorr respectively. To remove the residual gold mask, the sample was dipped into KI and I_2 mixture solution for 40 sec. The diameter and density of the fabricated sub-wavelength structures were nearly the same as those of the gold cluster masks, while the height was controlled by the etching time. The silicon nitride sub-wavelength structure fabricated with 90 sec etching time was with height of h = 88 nm and the total silicon nitride ARCs thickness was 200 nm. The morphology of SWS was analyzed by atomic force microscopy (AFM) and Scanning electron micrograph (SEM). The reflectance of the SWS were measured using an n-and-k analyzer (model: 1280, N-and-K Tech. Inc.).

B. *Simulation and Calibration*

A single pyramidal structure was first assumed for the reflectance calculation with respect to the wavelength for the simplicity. The etched Si_3N_4 and the thickness of the non-etched Si_3N_4 were the most two crucial designing parameters for the reflectance optimization. The SWS under study is a diffractive structures and its reflectance property could be calculated by a multilayer RCWA technique which is an exact solution of Maxwell's equations for the electromagnetic diffraction by grating structures [8].

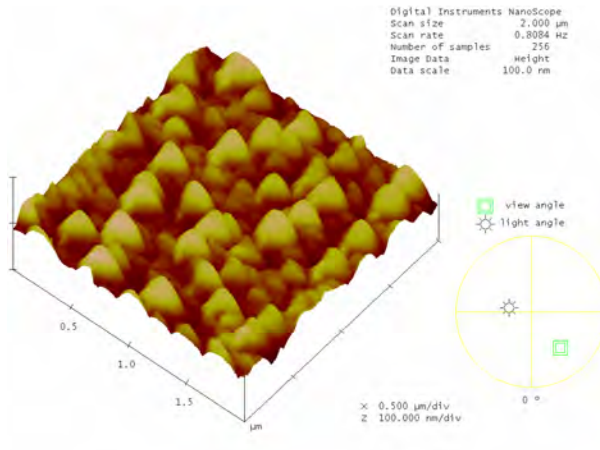
Simulated results of pyramidal structures with height of h = 88 nm and total silicon nitride ARCs thickness of 200 nm are compared with the results obtained from measurement which will be discussed below. The calibrated model of the refractive index of silicon n_{si} is given by

$$n_{Si} = y_0 + a\left(\frac{c-1}{c}\right)^{\left(\frac{1-c}{c}\right)}\left[\frac{\lambda - x_0}{b} + \left(\frac{c-1}{c}\right)^{\frac{1}{c}}\right]^{c-1} \times e^{-abs\left[\frac{\lambda - x_0}{b} + \left(\frac{c-1}{c}\right)^{\frac{1}{c}}\right]^{c} + \frac{c-1}{c}}, \qquad (1)$$

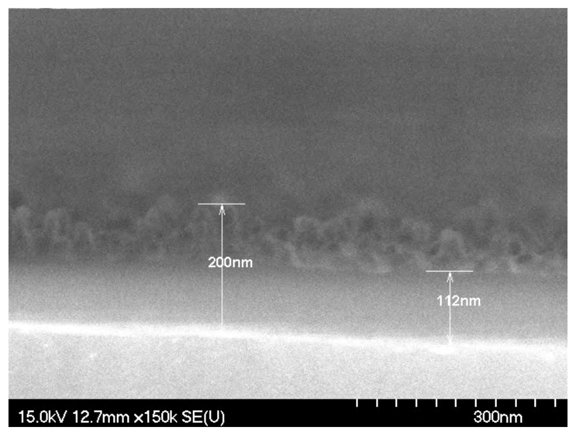
where λ is wavelength of the spectrum and the fitted coefficients are a = 0.7009, b = 145.3896, c = 1.5034, x_0 = 476.3470, y_0 = 4.2045 and R^2 = 0.9937 has been obtained for the best accuracy. Using the calibrated model, the height of sub-wavelength structure and the thickness of non-textured Si_3N_4 structures are optimized for the lowest reflectivity at wavelength of 630 nm. The reflectivity obtained from the optimized Si_3N_4 sub-wavelength structures are compared with the Si_3N_4 SLAR coatings and (MgF_2: SiN_x) DLAR coatings in terms of average residual reflectance (R_{av}). The reflectance data obtained from RCWA simulation of the optimized sub-wavelength structure is thus used to estimate the electrical data and efficiency by using PC1D [9].

III. Results and Discussion

The roughness of silicon nitride SWS was measured to be 10.4 nm from the AFM measurement. The observed optical effects are explained by the formation of a nanoscale SWS on the silicon nitride surface, representing an effective medium with a smooth transition of the refractive index from air to silicon nitride. From Figure 1(a), the etch depth was only several nm. So, it is expected that we can apply this technique to thin-film silicon solar cells. Figure 1(b) shows the cross-sectional views of the SEM image of the fabricated SWS on silicon nitride. From the figure 1(b), the height of the silicon nitride SWS was measured as 88 nm and the remained non-etched silicon nitride thickness was 112 nm. These values were taken as reference for the optimization of the SWS structures for the rest of the work. Figure 1(a) shows the AFM images of the silicon nitride SWS sample surface with RIE etching time of 90 sec.



(a)



(b)

Figure 1. Morphology of the fabricated Si_3N_4 SWS (a) AFM Image and (b) SEM Image.

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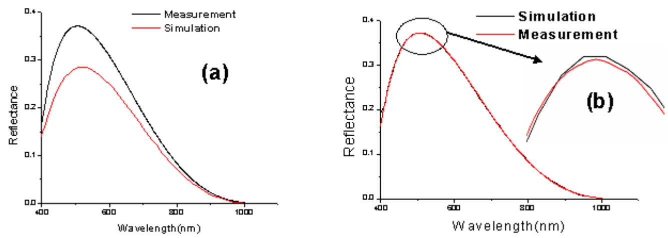
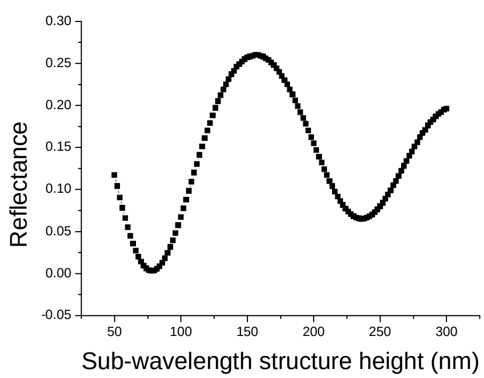
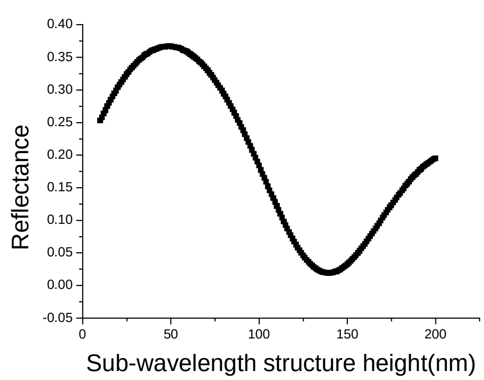


Figure 2. RCWA calculated specular optical reflectivity at normal incidence and measurement reflectivity for Si_3N_4 layer of thickness 200 nm deposited on silicon substrate of which 88 nm is the SWS height and 112 nm remained as non-etched. (a) Results with the constant silicon refractive index of 4.35. (b) Results with the silicon refractive index given by a calibrated equation.

The simulated results of pyramidal structures with height of h = 88 nm and total silicon nitride ARCs thickness of 200 nm are compared with the results obtained from measurement after using the calibrated model of equation 1 is shown in Figure 2(b). It has been found that the error between measurement and calculation has been reduced with R^2 = 0.9937 as seen in Figure 2(b).



(a)



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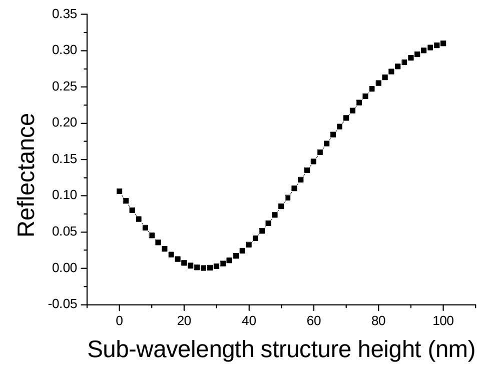

(c)

Figure 3. Calculated specular optical reflectivity at normal incidence at 630 nm wavelength to get the best Si_3N_4 SWS height for total Si_3N_4 thickness of (a) 300 nm (b) 200 nm (c) 100 nm.

Figure 3(a) shows the RCWA-modeled specular optical reflectivity with SWS height formed on silicon nitride with total thickness of 300 nm at normal incidence at 630 nm wavelength. It is clearly seen from figure 3(a) that lowest reflectance can be achieved with silicon nitride SWS height of 78 nm. Thus we can achieve a reflectance less than 1% for wavelength of 630 nm if we use a silicon nitride ARC on silicon and form a 78 nm SWS structure on it and 222 nm non-etched silicon nitride films. Similarly, we also optimized the other two cases with silicon nitride total thickness of 200 nm and 100 nm as shown in Figures 3(b) and 3(c) respectively. The optimized silicon nitride SWS thickness / non-etched silicon nitride thickness in these two structures for the above mentioned two cases were 140 nm / 60 nm and 24 nm / 76 nm respectively.

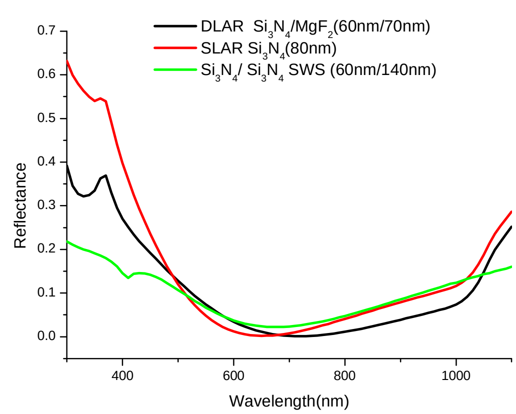

Figure 4. Example Specular optical reflectivity at normal incidence of optimized structures of Si3N4 SWS height of 140 nm and non-etched silicon nitride thickness 60 nm compared with silicon nitride SLAR (80 nm) and silicon nitride/magnesium fluoride DLAR (60 nm / 70 nm) structures.

The ability to predict the achievable residual reflectance level in AR coatings designed to operate in given spectral bands would be a great asset to thin film designers [10]. So, AR design is also characterized by its average residual reflectance R_{av}, which is defined by the equation

$$R_{av} = \frac{1}{\lambda_u - \lambda_l} \int_{\lambda_l}^{\lambda_u} R(\lambda) d\lambda, \qquad (2)$$

where, $R(\lambda)$ is the reflectance of the design and λ_l and λ_u are the lower and upper wavelength of the design window. Figure 4 compared the reflectance of several optimized structures with the optimized silicon nitride SLAR of thickness 80 nm and silicon nitride/MgF_2 DLAR of thickness 60 nm / 70 nm. The average residual reflectance R_{av} for the above three structures have been calculated using the equation 2 and the results are shown in Table 1. It is clear from Table 1 that the lowest R_{av} was obtained for DLAR structure and the highest R_{av} was for SLAR structure. Thus it clearly indicates that optimized silicon nitride structure with SWS will definitely give better performance than silicon nitride SLAR and will give a comparable performance with DLAR.

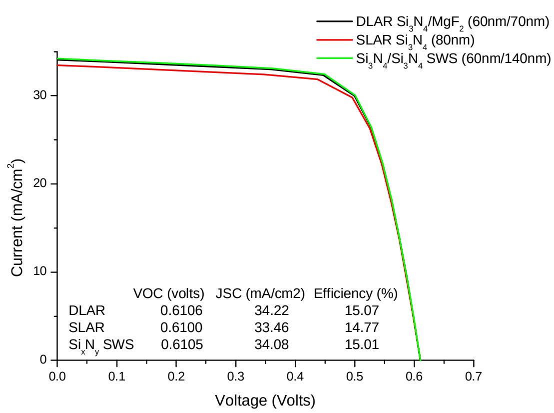

Figure 5. Example I-V curves of solar cells of optimized structures of Si_3N_4 SWS height of 140 nm and non-etched Si_3N_4 thickness 60 nm compared with Si_3N_4 SLAR (80 nm) and Si_3N_4 /magnesium fluoride DLAR (60 nm / 70 nm) structures obtained from PC1D simulation.

To confirm the performance of silicon nitride SWS structure, we simulated the solar cell performance using PC1D software. The reflectance spectra obtained from RCWA simulation were used in PC1D simulations to compare the effect on the short circuit current density (J_{SC}), open circuit voltage (V_{OC}) and efficiency (η) for a solar cell structure based on the standard PC1D template for a low cost silicon solar cell. The silicon material was set to p-type with resistively of 1.008 Ω-cm and a diffused emitter with error function distribution and 99.4 Ω / sq. emitter sheet resistances. The base contact had a resistance of 0.015 Ω and the cell had an internal shunt of 0.3 Siemens. The bulk life time was set to 7.03 μs with a back surface recombination velocity of 10^5 cm / s. The output characteristics and parameters obtained from PC1D for SLAR, DLAR and optimized silicon nitride SWS are shown in Figure 5. It is clear that though JSC value of optimized silicon nitride SWS is less than 80nm Si_3N_4 SLAR structure, V_{OC} and efficiency are more than silicon nitride SLAR structure as can be clearly seen from Figure 5.

TABLE I. AVERAGE RESIDUAL REFLECTIVITY FOR OPTIMIZED STRUCTURES OF 140 NM Si_3N_4 SWS AND 60 NM NON-TEXTURED Si_3N_4 FILM COMPARED WITH Si_3N_4 SLAR (80 NM) AND Si_3N_4 / MAGNESIUM FLUORIDE DLAR (60 NM / 70 NM) STRUCTURES.

ARC structure	Average residual reflectance R_{av} (%)
Si_3N_4 SWS	9.56
DLAR	10.68
SLAR	15.136

IV. CONCLUSION

We have fabricated Si_3N_4 sub wavelength structures using the mask less RIE technique for silicon. RCWA method was used to evaluate the optical properties of surface textures quantitatively. The reflectance data obtained from RCWA simulation of the optimized sub-wavelength structure has thus been used to estimate the electrical data and efficiency by using PC1D. Using the experimentally validated simulation, we have found there is a remarkable efficiency increase, about 0.2%, for the explored Si_3N_4 SWS with the height of 140 nm (i.e., the pyramidal part) and the non-etched layer of 60 nm, as compared with SLAR.

ACKNOWLEDGMENT

This work was supported in part by Taiwan National Science Council (NSC) under Contracts NSC-97-2221-E-009-154-MY2, NSC-97-2752-E-009-001-PAE and by Motech Industries Inc. (MOTECH), Tainan, Taiwan, under a 2008–2009 grant.

REFERENCES

[1] M. A. Green, “High Efficiency Silicon Solar Cells,” Trans Tech Publication, Aedermannsdorf, 1987.

[2] S. M. Sze, “Semiconductor Devices, Physics and Technology,” Wiley, New York, 1985.

[3] S. S. Strehlke, S. Bastide, J. Guillet and C. Levy-Clement, “Design of porous silicon antireflection coatings for silicon solar cells,” Mat. Sci. Eng. B, 2000, 69, pp. 81-86.

[4] D. H. Macdonald et al., Sol. Energy, “Texturing industrial multi-crytsalline silicon solar cells,” 2004, 76, pp. 277-283.

[5] Y. Inomata, Sol. Energy Mater. Solar Cells, “Surface texturing of large area multicrystalline silicon solar cells using reactive ion etching method,” 1997, 48, pp. 237-242

[6] H. F. W. Dekkers, F. Duerinckx, J. Szlufcik, J. Nijs, “Silicon surface texturing by reactive ion etching,” Opto-Elctron. Rev., 2000, 8, pp. 311-316.

[7] K. C. Sahoo, M.-K. Lin, E. Y. Chang, Y.-Y. Lu, C.-C. Chen, J.-H. Huang, and C.-W. Chang, Nanoscale Research Letters, in press. [http://dx.doi.org/ 10.1007/s11671-009-9297-7]

[8] K. C. Sahoo, Y. Li, and E. Y. Chang, Computer Physics Communications, in press. [http://dx.doi.org/10.1016/j.cpc.2009.04.013]

[9] D. A. Clugston and P. A. Basore, in: Proc. The 26th IEEE Photovoltiac Specialists Conf., Anaheim, 1997, pp. 207- 210.

[10] A. V. Tikhonravov, M. K. Trubetskov, T. V. Amotchkina, and J. A. Dobrowolski, “Estimation of the average residual reflectance of broadband antireflection coatings,” Applied Optics 2007, 47 C124-130.