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Description	

Passivation of textured crystalline silicon with small pyramids by silicon nitride films formed by catalytic chemical vapor deposition and phosphorus catalytic impurity doping

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Silicon nitride (SiN_x) films formed by catalytic chemical vapor deposition (Cat-CVD) and phosphorus (P) catalytic impurity doping (Cat-doping) are applied on textured crystalline silicon (c-Si) wafers with a pyramid size of 1–2 μm to reduce the surface recombination of minority carriers. SiN_x single layer passivation realizes a surface recombination velocity (SRV) of less than 10 cm/s. The addition of a P Cat-doped layer results in a reduction in a SRV to ~ 7 cm/s owing to field-effect passivation. These values are comparable to those obtained in our previous study for textured c-Si surface with larger-sized pyramids, indicating the high passivation ability of Cat-CVD SiN_x films and P Cat-doping independent of the size of pyramids. In addition to the double-side textured wafers, we also prepare a single-side textured wafer using Cat-CVD SiN_x as an etching barrier. We find that Cat-CVD SiN_x films can be utilized as an etching barrier against alkali solution, and a high effective minority carrier lifetime (τ_{eff}) of 2.3 ms has been obtained by the passivation with Cat-CVD SiN_x films. These

achievements will contribute to an improvement in the performance of back-contact c-Si solar cells.

Keywords: silicon nitride, catalytic chemical vapor deposition, catalytic impurity doping, back-contact crystalline silicon solar cell, texture

1. Introduction

Crystalline silicon (c-Si) solar cells have dominated the market share of photovoltaics [1], due to their matured fabrication technology, high long-term stability, and high efficiency. In recent years, back-contact c-Si solar cells have attracted considerable attention, in which all the electrodes and p–n junctions are formed on the rear-side surface and there are no electrodes on the illumination-side surface [2–8]. This leads to more light absorption due to no shading loss compared to conventional cells, resulting in higher short-circuit current density (J_{sc}). Furthermore, since the electrodes are located on the rear-side surface, wiring resistances can be small compared to conventional modules, and power loss originating from a series resistance can thus be reduced. On the other hand, a significantly high minority carrier lifetime is required for the back-contact solar cells. This is because minority carriers generated near the surface of the c-Si substrates need to diffuse to the electrodes on the rear-side surface. That is, a high bulk minority carrier lifetime (τ_{bulk}) and a low surface recombination velocity (SRV) are essential for high-efficiency back-contact c-Si solar cells.

Silicon nitride (SiN_x) films have a high passivation ability because of the termination of Si dangling bonds by hydrogen contained in the SiN_x films and positive fixed charges in the SiN_x by which the density of holes, minority carriers in n-type Si, is reduced near the c-Si surface. The optical loss can also be reduced since a SiN_x film has an antireflective effect. We have thus far investigated the formation of several types of passivation films on c-Si surfaces by catalytic chemical vapor deposition (Cat-CVD) [9–15]. Cat-CVD is a method of depositing thin films using radicals formed by decomposing gas molecules through catalytic cracking on a heated catalyzing wire [16,17]. Unlike in the case of plasma-enhanced CVD (PECVD), there is no plasma damage to substrates during Cat-CVD, leading to high passivation quality. For example, SiN_x /amorphous Si (a-Si) stacked films can realize an effective minority carrier lifetime (τ_{eff}) of ~ 10 ms and a SRV of < 1 cm/s on flat n-type Si(100) wafers [9,10,13]. A SiN_x single layer can also have an excellent passivation quality with a τ_{eff} of ~ 3 ms and a SRV of ~ 5

cm/s on flat n-type Si(100) wafers [12]. Besides, a Cat-CVD apparatus can be applied for the doping of phosphorus (P) or boron (B) to c-Si [18–29]. This technique, catalytic impurity doping (Cat-doping), can form a doping layer with an areal dopant density of $>10^{12}$ cm⁻² on a c-Si surface by exposing c-Si wafers to the decomposed species of PH₃ or B₂H₆ [15,19–25]. The profile of Cat-doped dopants has been shown elsewhere [23], in which the dopants are concentrated in the vicinity of c-Si surface within a depth of ~10 nm. By the existence of the highly doped ultra-thin layer, the density of minority carriers near the c-Si surface is significantly reduced, which leads to less recombination rate and larger τ_{eff} . An excellent τ_{eff} of ~7 ms and SRV of ~2 cm/s can be obtained on flat Si(100) wafers by combining Cat-CVD SiN_x and P Cat-doping [23].

To minimize the optical reflectance on c-Si solar cells, micrometer-sized pyramidal-shaped textures are generally formed on c-Si surfaces by anisotropic alkaline etching [30–38]. We have demonstrated that Cat-CVD SiN_x passivation films and P Cat-doping can be applied not only to flat c-Si substrates but also to the textured c-Si surfaces. Cat-CVD SiN_x films on textured c-Si surfaces realize a SRV of ~8.0 cm/s, and the combination of SiN_x and P Cat-doping leads to a SRV of ~6.7 cm/s [15]. These results have been obtained for textured c-Si wafers with an average pyramid size of ~10 μm formed through a conventional alkaline solution process. Recently, advanced alkali solution to form smaller and more uniform pyramids has been established containing sophisticated additives to control the formation of the tips of the pyramids [39,40]. The usage of the advanced alkaline solution results in the formation of pyramids with an average size of 1–2 μm and a better anti-reflection effect than conventional textured c-Si wafers. On such small-sized pyramids, Cat-CVD SiN_x films might show different passivation ability, and for the industrial application of Cat-CVD SiN_x films, sufficiently high (SRV<10 cm/s) passivation ability on the small-sized pyramids must be achieved.

In this study, we have attempted to utilize Cat-CVD SiN_x films and P Cat-doping for the passivation of c-Si surfaces with small-sized pyramids to realize the low SRV. We also prepared

a single-side textured substrate by using Cat-CVD SiN_x as an etching barrier layer against alkali solution. This aims at the application to the fabrication process of back-contact solar cells, which generally have pyramids only on an illumination side.

2. Experimental methods

We used 290- μm -thick mirror-polished n-type Si(100) wafers with a resistivity of 1–5 Ωcm and a τ_{bulk} of >10 ms. We first cleaved them into 2×2 cm^2 -sized pieces. The substrates were first cleaned in ozone water for 5 min. The wafers were put in KOH-based alkali solution with organic additives, SE-2000H, for 15 min at 90 °C to form Si(111)-faceted small pyramids through anisotropic etching. After the texturing process, we performed ultrasonic cleaning in ozone water for 5 min, followed by RCA cleaning in which we used $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$ solution (SC-1) for 15 min for the removal of organic additives and then $\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$ solution (SC-2) for 15 min to remove metallic contaminants.

SiN_x films were then deposited on the textured c-Si surfaces by Cat-CVD under the condition summarized in Table I. The SiN_x films deposited under this condition on flat Si substrates showed a thickness of ~ 100 nm and a refractive index of ~ 2.0 , based on the measurements by spectroscopic ellipsometry (J. A. Woollam Co., WVASE32). The sample was finally annealed in nitrogen atmosphere at 350 °C for 30 min to improve their passivation quality by the termination of dangling bonds by hydrogen atoms supplied from the SiN_x films [12,14]. We also prepared a flat c-Si substrate passivated with Cat-CVD SiN_x films for comparison.

We also additionally performed P Cat-doping for the part of textured c-Si substrates before SiN_x deposition under the condition summarized in Table I. After the Cat-doping, the sample was annealed in nitrogen atmosphere at 350 °C for 30 min [23]. SiN_x films were then deposited on both sides of the textured c-Si substrate by Cat-CVD under the condition summarized in Table I. The samples were finally annealed again in nitrogen atmosphere at 350 °C for 30 min.

To apply the textured c-Si substrates for the back-contact c-Si solar cells, in which all the electrodes are fabricated on the rear side, we prepared a single-side-textured c-Si substrate passivated with Cat-CVD SiN_x films, whose process flow is schematically shown in Fig. 1. A SiN_x film was first deposited on the rear surface of c-Si substrates by Cat-CVD under the condition summarized in Table I to protect the back surface of c-Si against alkali solution. We then performed the anisotropic alkali etching for the substrate on one side through the same steps as the double-side texturing. The rear-side SiN_x film was then removed by dipping in 5% HF, followed by ultrasonic cleaning in ozone water for 5 min and RCA cleaning. After that, SiN_x films were deposited again on both sides of the c-Si substrate by Cat-CVD under the condition summarized in Table I.

The morphology of a textured Si surface was observed by scanning electron microscopy (SEM) (JEOL JSM-7900F). The optical reflectance spectra of a textured c-Si was measured in a spectrophotometer (Shimadzu UV-3150) equipped with an integrating sphere. The passivation quality of the SiN_x films was characterized by measuring effective minority carrier lifetime (τ_{eff}) by microwave photoconductivity decay (μ -PCD) (KOBELCO LTA-1510 EP). For the μ -PCD measurement, we used a pulse laser with a wavelength of 904 nm and a photon density of $5 \times 10^{13} \text{ cm}^{-2}$, roughly corresponding to an excess carrier density of $1 \times 10^{15} \text{ cm}^{-3}$, for the excitation of minority carriers. The SRVs of the SiN_x/c-Si interfaces were calculated by using the following equation:

$$\tau_{\text{eff}}^{-1} = \tau_{\text{bulk}}^{-1} + (S_{\text{front}} + S_{\text{rear}})/W, \quad (1)$$

where S_{front} , S_{rear} , and W represent front-side and rear-side SRVs and c-Si thickness, respectively. The second and third terms of the right-hand side of eq. (1) can be unified to be $2S/W$ for the symmetric structures with the common SRV, S , on both sides. Since the τ_{bulk} of the wafers used in this study is sufficiently high (>10 ms), the term τ_{bulk}^{-1} can be neglected, and SRVs were thus obtained simply from τ_{eff} and W .

3. Results and discussion

3.1 Formation of pyramidal-shaped textures

Figs. 2(a) and 2(b) show the cross-sectional and plan-view SEM images of the textured c-Si surface. One can see 1–2 μm -sized uniform pyramids, which are significantly different from the pyramids with a typical size of $\sim 10 \mu\text{m}$ formed through alkali etching using conventional solution [15]. It should be emphasized that the usage of the advanced alkali solution contributes not only to the formation of pyramids on c-Si with smaller size and higher uniformity but also to the shortening of the texturing duration and to a reduction in Si loss by etching. These properties are appropriate for the mass production of c-Si solar cells, particularly for the cells with thin ($\sim 100 \mu\text{m}$) wafers.

Fig. 3 shows the optical reflectance spectra of the textured c-Si substrates without SiN_x coating. A remarkably lower optical reflectance is obtained on the c-Si surface with pyramids formed in the advanced alkali solution, compared to the c-Si surface textured by conventional alkali solution [15]. This is a clear indication of the advantage of the small pyramids with high uniformity. The reflectance of c-Si can be further reduced by depositing a SiN_x antireflection film, as also shown in Fig. 3.

3.2 Passivation of c-Si surfaces by Cat-CVD SiN_x

Fig. 4 shows a typical example of τ_{eff} mapping, in which the result of the single-side textured structure is seen, measured by $\mu\text{-PCD}$ within $1.4 \times 1.4 \text{ cm}^2$ area of the sample. We see higher τ_{eff} near the center of the sample and lower τ_{eff} near the edges. The lower τ_{eff} near the edges is because of the existence of unpassivated regions. The Cat-CVD apparatus used in this study is a face-down-type system, and the edge regions of the $2 \times 2 \text{ cm}^2$ -sized substrates are not covered with SiN_x films due to the shape of a sample holder. The unpassivated regions have considerably high SRVs, on which minority carriers generated near the edges recombine. Hence,

SRVs calculated from the τ_{eff} values obtained near the edges underestimate the passivation quality of SiN_x films. We thus use the τ_{eff} values obtained around the center of the samples.

Fig. 5 shows the τ_{eff} values for c-Si substrates passivated with SiN_x films after the post-deposition annealing for different structures—flat, double-side-textured, and single-side-textured c-Si substrates. The SRV values for the samples are also indicated in Fig. 5. Note that all the samples showed τ_{eff} of much less than 1 ms before the post-deposition annealing. The significant improvement in τ_{eff} by the post-deposition annealing is due to the termination of dangling bonds on c-Si surfaces by hydrogen atoms supplied from the SiN_x films [14]. A τ_{eff} of ~ 2.6 ms is obtained for the flat substrate passivated with SiN_x films, corresponding to a SRV of ~ 5.6 cm/s calculated by using Eq. (1). This value is almost comparable to that obtained in our previous study [12]. The double-side textured substrate shows a τ_{eff} of ~ 1.6 ms, corresponding to a SRV of ~ 9.1 cm/s, which is smaller than the SRV of the flat one of ~ 5.6 cm/s. The lower τ_{eff} for the textured substrate may be partly due to an increase in the surface area of c-Si by the formation of pyramids. Another possible reason is that the textured c-Si surface receiving alkali treatment has more metal and/or organic contaminants which might not be removed completely by the RCA cleaning. Note that the SRV of ~ 9.1 cm/s is still remarkably high and is almost the same as that obtained for the textured c-Si with pyramids with a size of $10\ \mu\text{m}$ (~ 8 cm/s) [15]. This fact indicates that Cat-CVD SiN_x films universally have high passivation ability, independent of the size of pyramids on textured c-Si.

The τ_{eff} of the double-side-textured c-Si substrate increases to ~ 2.0 ms, corresponding to a SRV of ~ 7.3 cm/s, by the addition of P Cat-doping. This is probably due to the formation of ultra-thin (~ 10 nm) highly P-doped region near the c-Si surface, which enhances field-effect passivation [23]. The SRV value obtained is almost equivalent to that of SiN_x/P Cat-doped c-Si interfaces with $10\text{-}\mu\text{m}$ -sized pyramids (~ 6.7 cm/s) [15]. This clearly indicates the effectiveness of P Cat-doping also on textured c-Si surfaces with $1\text{--}2\ \mu\text{m}$ -sized small pyramids. Unlike in the case of additional film deposition such as a-Si, P Cat-doping can improve a SRV

without an increase in optical loss by parasitic absorption, and is thus suitable for the passivation of the illumination side of back-contact c-Si solar cells.

For the application of the textured wafers with small-sized pyramids to back-contact solar cells, we also prepared a single-side-textured substrate passivated with SiN_x films through the processes shown in Fig. 1. The single-side-textured substrate shows a τ_{eff} of ~ 2.3 ms. Assuming a SRV of ~ 5.6 cm/s for the flat surface obtained from the double-side mirror-polished sample, the SRV of the textured surface passivated with Cat-CVD SiN_x films can be estimated to be ~ 7.0 cm/s from Eq. (1). The τ_{eff} and SRV values are much better than those for the double-side-textured sample. The reason for the better SRV is unclear at present. Spectroscopic ellipsometry measurements revealed that only less than 10 nm of SiN_x is lost during 15-min alkali texturing process at 90 °C. This means that Cat-CVD SiN_x films can also be utilized as etching barriers against alkali solution.

We have clarified that Cat-CVD SiN_x and P Cat-doping can realize sufficiently low SRVs of much less than 10 cm/s on the surfaces of textured c-Si with small-sized pyramids. The utilization of the textured c-Si wafers with small-sized uniform pyramids can also lead to a reduction of optical reflectance compared to the c-Si with larger-sized pyramids formed by conventional texturing process. The formation of back-contact cells exhibiting a higher J_{sc} without a reduction in an open-circuit voltage will thus be expected by using c-Si wafers with the small-sized pyramids in the future.

4. Conclusions

We have demonstrated the high passivation ability of Cat-CVD SiN_x films on textured c-Si surfaces with 1–2 μm -sized uniform pyramids with an excellent anti-reflection effect. The passivation quality is significantly improved by adding a P Cat-doping layer before the deposition of a Cat-CVD SiN_x film. We have also prepared a single-side-textured c-Si sample passivated with SiN_x films, which show a τ_{eff} of as high as ~ 2.3 ms. The obtained results show

that Cat-CVD and P Cat-doping have a potential to realize superior passivation for high-efficiency c-Si solar cells, especially for back-contact c-Si solar cells.

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Figure Captions

Fig. 1. Process flow of single-side-textured c-Si with SiN_x films: (a) SiN_x deposition on one side, (b) Texturing in alkali solution, (c) Removal of SiN_x by HF, (d) SiN_x deposition on both sides.

Fig. 2. (a) Cross-sectional and (b) plan-view SEM images of a textured c-Si surface.

Fig. 3. Reflectance spectra of textured c-Si wafers formed by using advanced and conventional alkali solution [15]. The reflectance spectrum of textured c-Si formed in advanced alkali solution with a SiN_x film is also shown.

Fig. 4 τ_{eff} mapping data measured by μ -PCD for the single-side textured structure.

Fig. 5 τ_{eff} values for c-Si substrates with flat, double-side-textured, and single-side-textured surfaces. The corresponding SRV values calculated from Eq. (1) are also shown.

Table I Conditions for SiN_x deposition and P Cat-doping.

	Substrate holder temperature (°C)	Catalyzer temperature (°C)	Duration (s)	Pressure (Pa)	Gas flow rate (sccm)
SiN _x deposition	100	1800	190	10	NH ₃ : 150 SiH ₄ : 8
P Cat- doping	80	1300	60	1	2.25% PH ₃ : 20 (He-diluted)

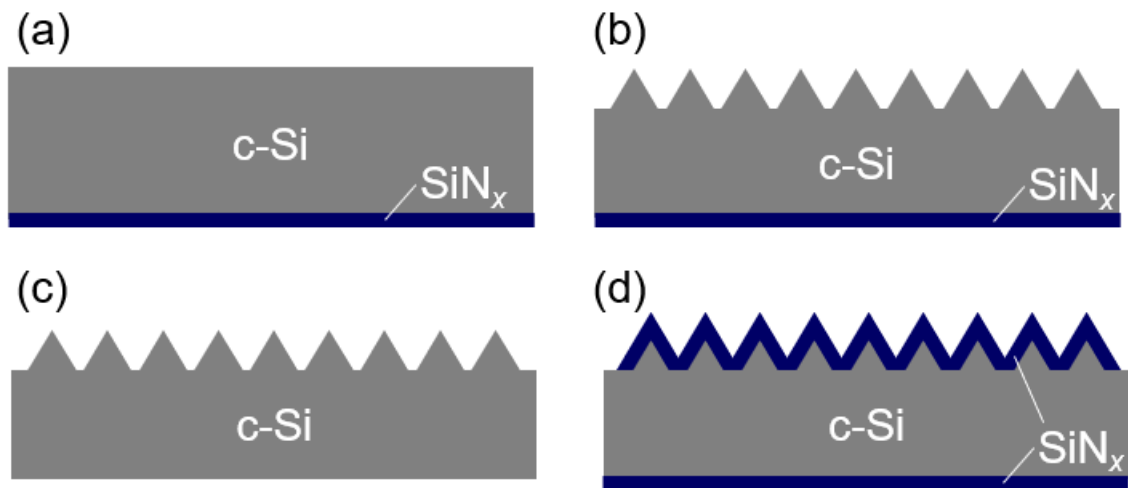


Fig. 1. (Color online) J. Liu et al.,

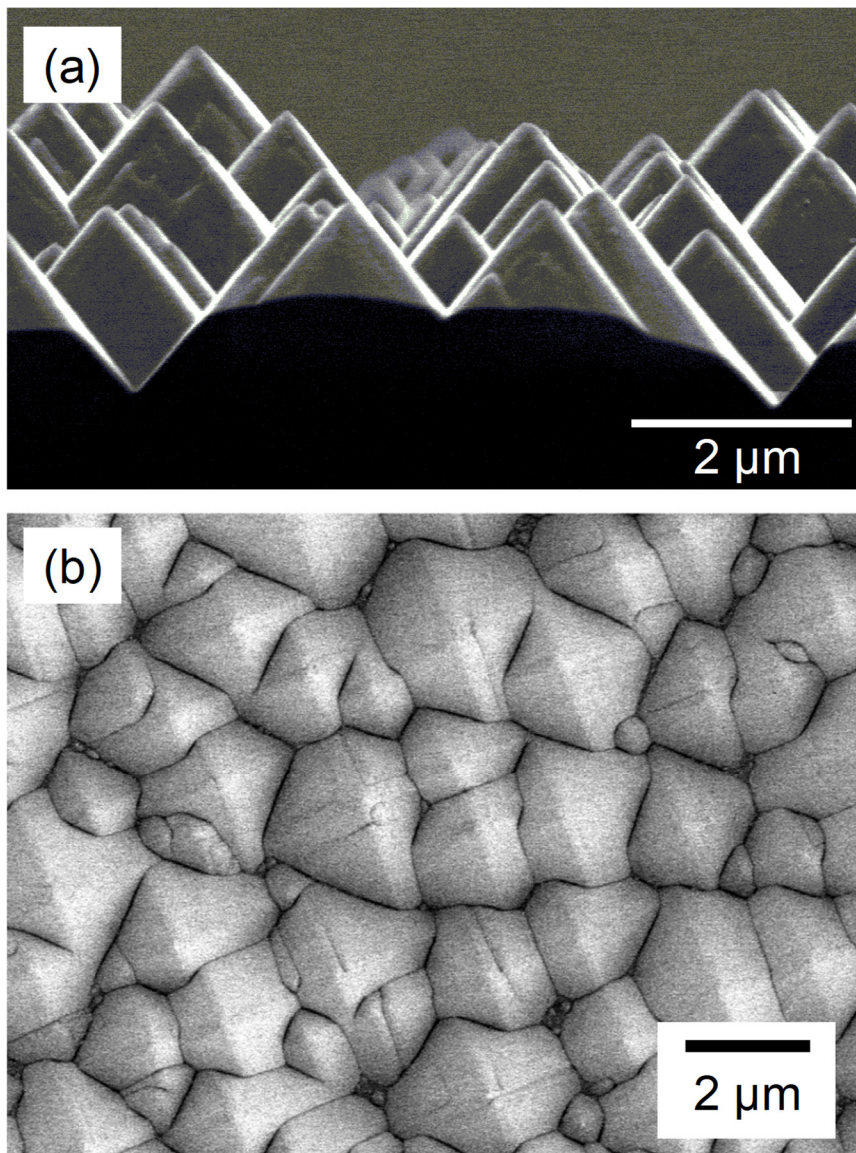


Fig. 2. (Color online) J. Liu et al.,

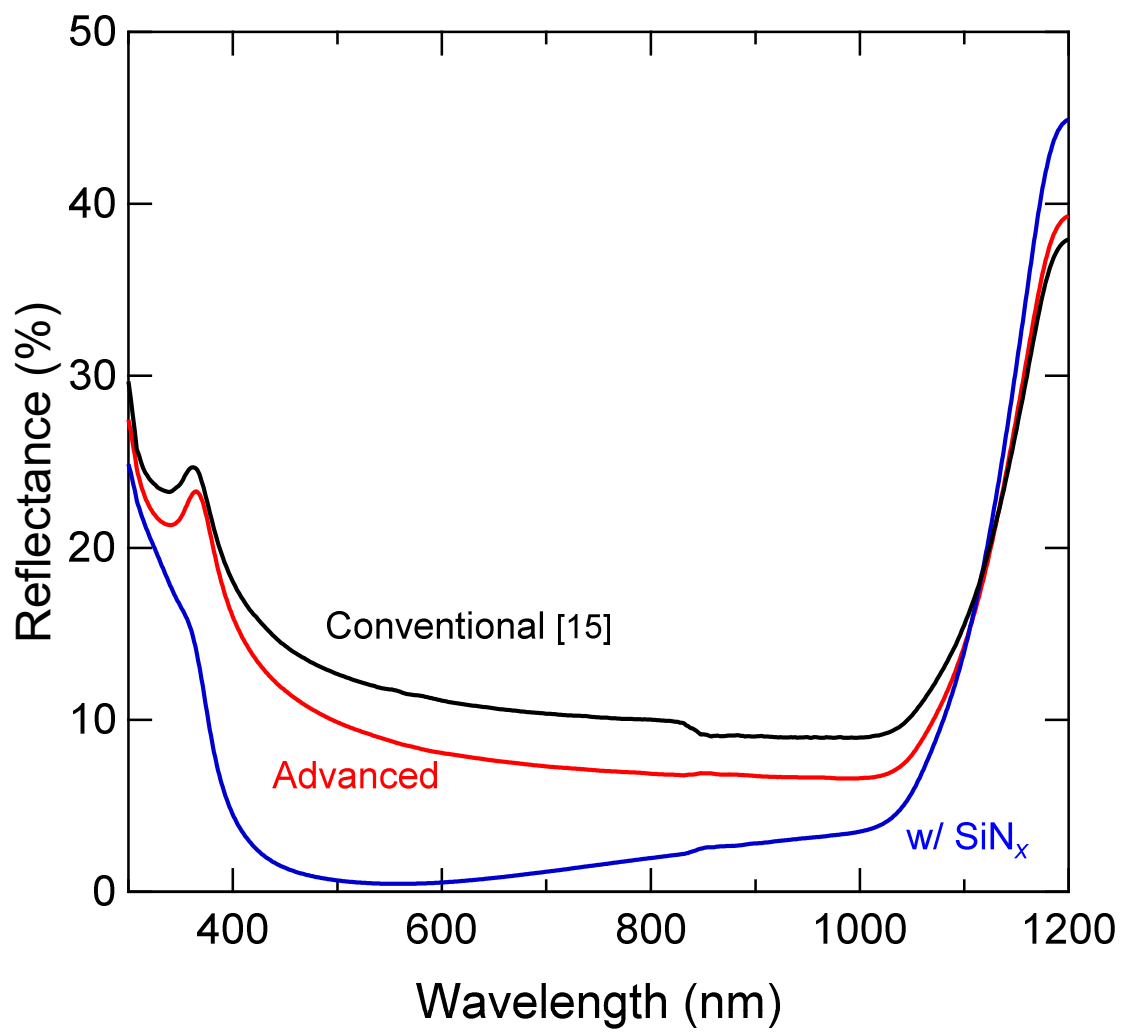


Fig. 3. (Color online) J. Liu et al.,

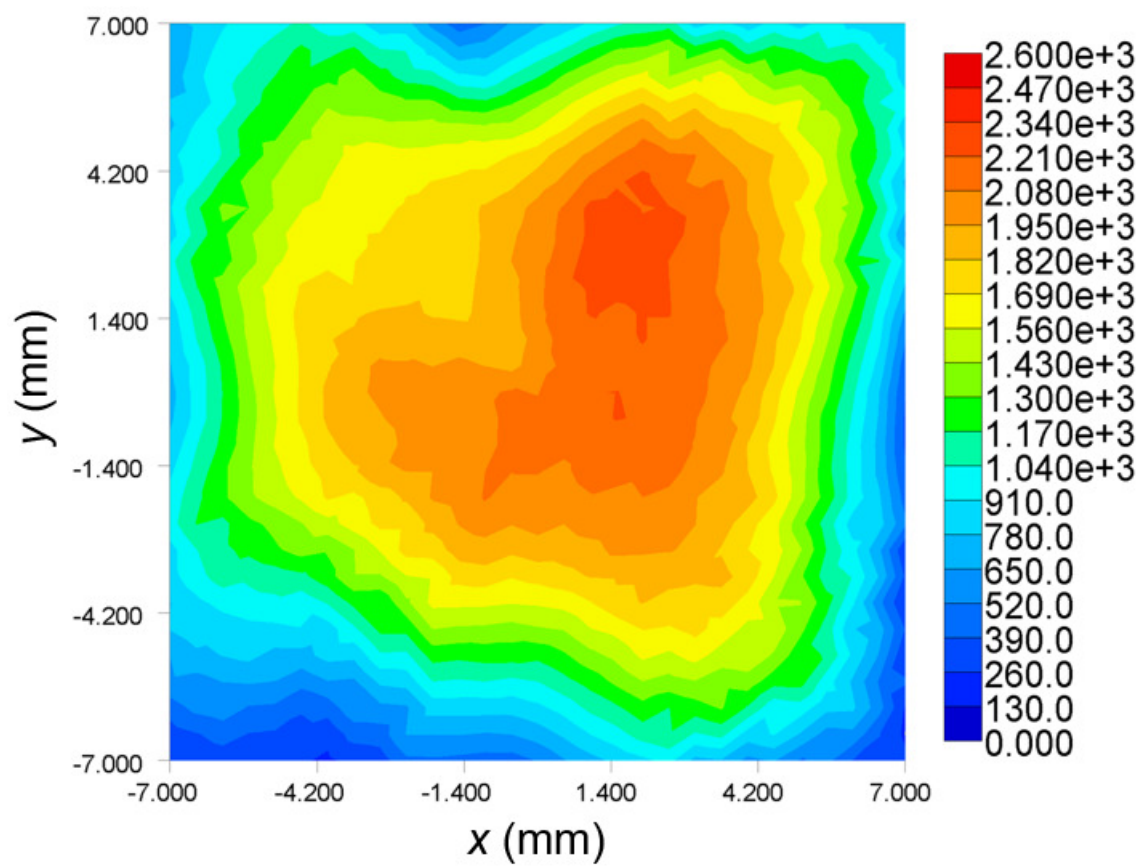


Fig. 4 (Color online) J. Liu et al.,

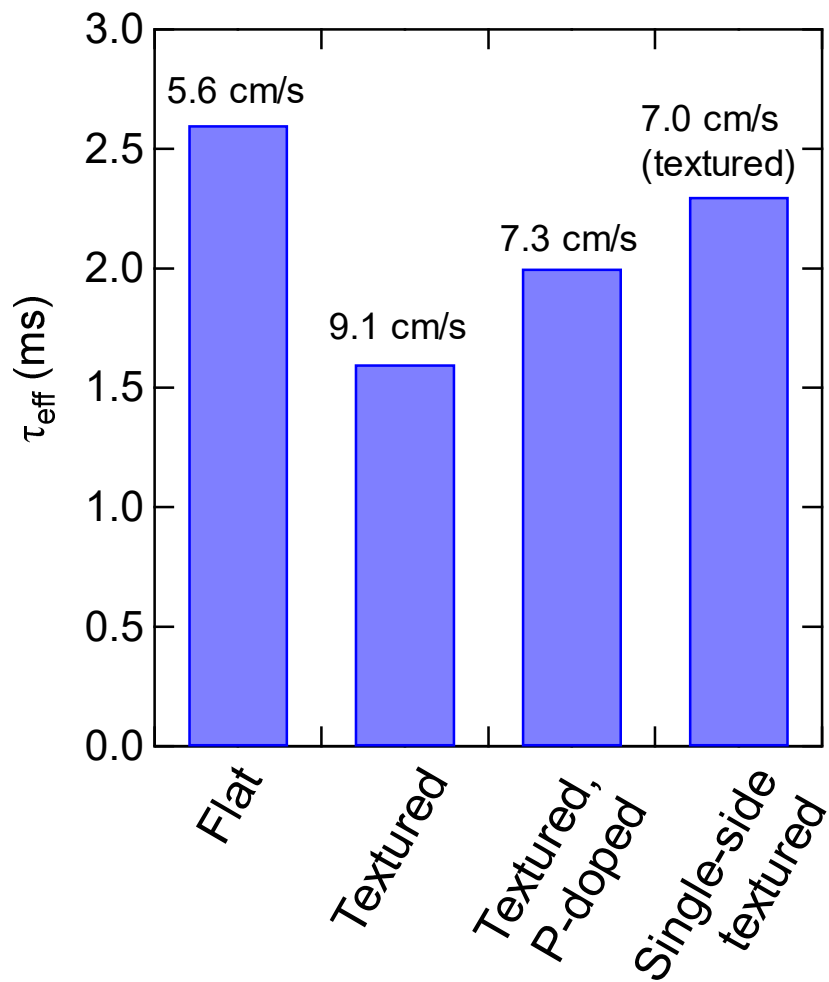


Fig. 5 (Color online) J. Liu et al.,