Transparent gold nano-membranes for the enhanced light trapping of the indium tin oxide films

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Abstract: A facile and scalable method for enhancing the light trapping effect of indium tin oxide films on photovoltaic devices is demonstrated. The Langmuir Blodgett technique is introduced to fabricate gold nano-membranes on the photovoltaic solar cells. Textured structures on the indium tin oxide films are created with the nano-membrane, producing effective surface roughness for significantly improved light trapping. As a result, the quantum efficiency of the solar cell integrated with the nano-membrane textured indium tin oxide film is enhanced over a broadband wavelength range, which leads to a 13% enhancement on the photocurrent density and an 8% efficiency enhancement.

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References and Links


1. Introduction

Indium tin oxide (ITO) thin films have been widely used as transparent electrodes on various photovoltaic (PV) devices due to the superior optical transmittance and electrical conductivity to other types of transparent conductive films [1–5]. For most of the PV devices that ITO is applied on, the energy conversion efficiency is mainly limited by the insufficient light absorption of the active layers [5–7]. Light trapping is increasingly important especially when the PV devices are made thinner in order to reduce the material costs. To address this issue, one has developed two light trapping mechanisms for PV devices built on ITO films: (i) refractive index matching to enhance the anti-reflection effect [1,8,9]; and (ii) generation of roughened surface morphology on ITO films to enhance the scattering effect and increase the light path length within the active layers [10–12]. For approach (i), the anti-reflection effect can be only achieved at a relatively narrow wavelength range due to the nature of destructive
interference. On the other hand, approach (ii) can achieve a broadband light absorption enhancement in PV devices.

A variety of methods have been reported for creating textured structures on ITO films. One typical way is to dry-etch the ITO films by inductively coupled plasma with an etching mask [11,13–16]. However, this method includes high-cost, toxic equipment and complex processes. More importantly, dry-etching could result in a degradation of the electrical property of the PV devices due to the introduction of defect states on the surface of the active layer [14,17]. Though one-step wet chemical processes have been reported to etch the as-deposited ITO films, these methods either require the ITO films to be polycrystalline [18,19] or include high temperature annealing up to 600 °C [20], which could be incompatible with certain types of PV devices and increase the energy consumption in producing the texturing on the ITO films. Other etching-free methods, such as two-step holographic lithography [21] and nanomoulding [22,23], have been reported; but the processes are complex and have yet to be proved for large-scale production.

In this paper, we demonstrated the use of a gold nano-membrane (AuNM) to achieve effective texturing of the ITO film on PV devices. As a proof-of-concept example, crystalline silicon wafer cells were selected, but our method could also be extended to other types of PV devices. We first introduced the Langmiur Blodgett (LB) technique as a fast and easy approach to fabricate the AuNM and transfer it onto the top surface of the solar cell. The ITO film was then deposited on top of the AuNM. The surface morphology of the AuNM/ITO integrated film was characterized by an atomic force microscope (AFM) to understand its texturing feature. The spectral measurement was carried out to study the optical behaviors of the AuNM/ITO integrated film in the solar cells, which were confirmed by the finite-difference time-domain (FDTD) simulation. The external quantum efficiency (EQE) and the I-V characteristics of the solar cells were performed to further reveal the enhanced light trapping effect of the AuNM/ITO integrated film on the performance of the solar cells.

2. Experiments

The planar single-crystalline silicon wafer solar cells were fabricated prior to the deposition of the AuNM. A p-type base/n-type emitter junction was formed by phosphorus diffusion into the saw damage etched boron-doped silicon wafers (2 cm × 2 cm × 180 μm). The aluminium paste was screen-printed onto the p-type side of the wafer and fired at ~800 °C to form a rear contact and a back surface field. The front contact on the n-type side was formed by depositing metal films (Ti 10 nm/ Pd 35 nm/ Ag 500 nm in sequence) in the pattern of gridlines through a lift-off photolithography process.

The AuNM was then fabricated by the LB technique following a method that we have recently reported [24]. In brief, firstly, the single-crystalline ultrathin gold nanowires (AuNWs) were synthesized by a fully solution-processed, one-step approach at the room temperature. The as-prepared AuNWs had a diameter of ~2.5 nm and a length up to tens of micrometers, leading to a super large aspect ratio of more than 10000 and high flexibility. Figures 1(a - e) show the schematic diagrams of the fabrication processes of the AuNM and the deposition onto the solar cell. One droplet of the AuNW dispersion in chloroform was spread onto the water surface in the LB trough (Fig. 1(a)). The AuNWs were distributed uniformly on the water surface immediately, forming a free-floating AuNM (Fig. 1(b)). Figure 1(c) shows the TEM image of the as-fabricated AuNM. The covering density of the AuNM could be well controlled by adjusting the distance between the two LB barriers and monitored via the surface pressure. By gently attaching the front surface of the solar cell with the solution surface (Fig. 1(d)), the AuNM could be easily transferred onto the solar cell when it was pulled away (Fig. 1(e)). Figure 1(f) shows the enlarged schematic structure of the solar cell integrated with the AuNM. The LB produced AuNMs can have a high uniformity and a controllable covering density at a large scale up to 300 cm² (depending on the area of the LB trough), which cannot be achieved by other deposition methods such as drop-casting [24] or
Furthermore, due to the ultrathin nature of the AuNWs, AuNMs are highly transparent, flexible and mechanically strong [24], which means they can be conformably attached to substrates and devices with any surface conditions.

Thereafter, a layer of the ITO film was deposited on the top of the AuNM by radio-frequency (RF) magnetron sputtering at the room temperature. The composition of the ITO target was 90% In$_2$O$_3$ and 10% SnO$_2$ by weight. The chamber pressure was evacuated to 5 × 10$^{-6}$ Torr before the argon gas was injected into the chamber. During the deposition, the RF power was kept at 120 W and the chamber pressure at 5 mTorr. The deposition time was 3 minutes. The solar cells with and without the AuNM (reference solar cell) were deposited with ITO films in the same batch, labeled as Cell A and Cell B, respectively. Figures 1(g) and 1(h) show the schematic structures of the fabricated solar cell with the AuNM/ITO integrated film, and the reference solar cell, respectively.

The thickness and the refractive index of the ITO films were measured by an ellipsometer. The surface morphology of the AuNM, ITO film and AuNM/ITO integrated film on the solar cells was characterized by AFM and scanning electron microscopy (SEM). The $EQE$, reflectance and $I-V$ curves of the solar cells were measured at each step of the fabrication process. FDTD simulations were performed by the Lumerical FDTD Solutions software [26].

3. Results and discussion

Figures 2(a) to 2(c) show the SEM images of the AuNM, ITO film and AuNM/ITO integrated film on the solar cells, respectively. The AuNM appears as parallel AuNW bundles that are highly aligned on the substrate. For the ITO film deposited on the bare silicon, a relatively flat surface is observed. When the ITO film is deposited onto the AuNM, wrinkle-like texturing of the ITO along the AuNW bundles is formed as shown in Fig. 2(c). Since the ITO films are too thin to be characterized by the SEM for cross-sectional view, the enhanced texturing effect on the ITO film by the AuNM is revealed by the AFM images as given in Figs. 2(d)–2(f) for the corresponding films. The root mean square surface roughness ($R_q$) of the AuNM and ITO film on bare silicon is 0.78 nm and 1.86 nm, respectively. However, as high as 8.17
nm $R_g$ of the AuNM/ITO integrated film can be achieved, which is three times larger than the addition of the above two values. Instead of forming a surface based on the morphology of the AuNM, the AuNM/ITO integrated film turns out to form tapered-range texturing with the base width around 100 nm and height around 30 nm, as revealed from the 1-D profile of the range extracted from the AFM image at the specified position (Fig. 2(g)). The main orientation of the ranges is the same as that of the original AuNM. This feature is attributed to the fact that during the sputtering process, the bombardment of the Ar ion and the plasma induced locally-high temperature could cause the ultrathin AuNWs to reshape into larger and rougher bundles. As a result, the roughness of the AuNW/ITO integrated film could be significantly increased.

Now it is essential to understand the optical behaviors of the textured AuNM/ITO integrated film. Figure 3(a) shows the measured reflectance of Cell A (with ITO + AuNM) and Cell B (with ITO). The reflectance of a bare solar cell (without ITO and AuNM) is also given as a benchmark. For Cell B, the decrease of the reflection was mainly due to the destructive interference between the light reflected from the air/ITO and ITO/silicon interfaces, resulting in an anti-reflection effect. The thickness of the ITO film was measured to be 26 nm, and the real part of the refractive index in the range of 1.7 ~2.0. These features caused the reflection minima to occur around the wavelength of 200 nm, beyond the wavelength range measurable with the spectrometer. For Cell A, a broadband reflection decrease compared to Cell B was observed over the wavelength range of 350 ~1100 nm, with the reflection minima red-shifting to 440 nm. The physical mechanisms of the enhanced light trapping can be attributed to three reasons. Firstly, the light path length in the textured AuNM/ITO integrated film is increased, which causes the destructive interference to occur at a longer wavelength. Secondly, the tapered structure (Fig. 2(g)) of the AuNM/ITO ranges can form refractive index gradient, i.e., the effective refractive index is gradually decreased from the bottom to the top [11]. Indeed, from the ellipsometry measurement, the overall refractive index of the AuNM/ITO integrated film is decreased compared to that of the flat ITO film. Meanwhile, the effective thickness of the AuNM/ITO integrated film is increased (60 nm as
measured by the ellipsometry) due to the height of the ranges. Thirdly, the nano-texturing on top of the cells could enhance the forward scattering from the AuNM/ITO integrated film, which means that the light path length in the silicon is increased, enabling the enhanced light absorption in the silicon. It is expected that the anti-reflection effects of the AuNM/ITO integrated film can lead to an additional light trapping mechanism due to the nano-texturing when combined with the conventional micrometer sized pyramid texturing for silicon solar cells [27].

![Graph](image)

**Fig. 3.** (a) Measured reflectance (solid lines) of a bare solar cell, Cell A with ITO + AuNW and Cell B with ITO. The dashed lines represent the FDTD simulated reflectance for the corresponding cases. (b) Simulated transmittance ($T$) and absorbance ($A$) of the ITO film and AuNM/ITO integrated film on silicon.

To confirm the measured features in Fig. 3(a), we perform the FDTD simulations. The refractive indices and the thicknesses of the ITO film on cell A and the AuNW/ITO integrated film on Cell B measured by the ellipsometry were input into the FDTD simulation. Periodic boundary condition is applied on the lateral direction (parallel to the silicon surface) to simulate ITO films with infinite area, and perfectly matched layer condition is applied on the vertical condition (perpendicular to the silicon surface) to avoid interference effects. As presented in Fig. 3(a), good fitting between the experimentally measured (solid lines) and simulated (dashed lines) reflection of the bare silicon and the ITO films on silicon is obtained, indicating the high accuracy of the model. The slight deviation between the measured and simulated reflection at wavelengths above 1000 nm is due to the semi-infinite consideration in the model that assumes all the light entering the silicon is absorbed, while in reality, part of the light is reflected back into the air from the rear surface. Figure 3(b) shows the simulated transmittance ($T$) and absorbance ($A$) of the ITO and AuNW/ITO integrated films on silicon from the model. It can be seen that the reflection decrease of the ITO films in the shorter wavelengths below 500 nm is partly due to the absorption of the films. For the AuNW/ITO integrated film, the absorption is larger as a result of the increased film thickness compared with the ITO film. This accounts for the decreased transmittance of the integrated film below 400 nm. Nevertheless, the absorption of both the ITO films is negligible in the longer wavelengths, and the transmittance of the AuNW/ITO integrated film is enhanced in a broadband range above 400 nm compared to that of the ITO film due to the enhanced anti-reflection effects. It should be pointed out that unlike other metallic nano-structures which can generate significant plasmonic effects on PV devices [6,26,28–31], the plasmonic absorption and scattering of the ultrathin AuNWs are too weak to induce noticeable change on the optical behaviors of the ITO film.
In order to reveal the effect of the improved anti-reflection behavior of the textured AuNM/ITO integrated film, we carried out the EQE measurement of the solar cells. To explicitly show the light trapping effect from the AuNM/ITO integrated film on the solar cells, we used planar cells without the conventional surface texture, leading to a relative low EQE and efficiency compared to the typical single-crystalline silicon wafer solar cell. Figure 4(a) shows the EQE curves of the bare cell, Cell A and Cell B. Consistently, due to the enhanced anti-reflection effect as described above, a broadband increase of the EQE enhancement for Cell A is observed, compared with Cell B, in the wavelength range of 400 – 950 nm. To further confirm the anti-reflection mechanisms in this range, the EQE enhancement (defined by \((\text{EQE}_{\text{sample cell}} - \text{EQE}_{\text{bare cell}}) / \text{EQE}_{\text{bare cell}}\)) curves of Cell A and Cell B are presented in Fig. 4(b). For Cell B, more EQE enhancement is observed at 400 – 600 nm, and the curve is flattened in the longer wavelengths, which is in accordance with the transmittance curve in Fig. 3(b). For Cell A, an EQE enhancement peak occurs at ~550 nm, matching well with the transmittance peak in Fig. 3(b). However, this EQE peak is less significant as revealed by the transmittance peak because of the week response of solar cells in the short-wavelength (300 – 500 nm) range originated from the heavily-doped emitters. In the wavelength range below 400 nm, the EQE is decreased for both cells due to the absorption of the ITO film. For Cell A, the EQE decrease is larger because of more reflection that is induced by the red-shifting of the reflection minima as well as more absorption in ITO. However, the EQE decreases occur where the power of the solar spectrum is relatively small. Hence, the overall optical performance enhancement of Cell A is not compromised. By integrating the EQE with the air mass 1.5 global (AM1.5G) solar spectrum, the photocurrent density \((J_{SC})\) of Cell A is increased from 24.79 mA/cm\(^2\) to 28.06 mA/cm\(^2\), with an enhancement of 13%. This is 5% higher than Cell B, whose \(J_{SC}\) is increased to 27.17 mA/cm\(^2\).

The EQE and \(J_{SC}\) enhancement is confirmed by the \(I-V\) measurement. Finally, the efficiency of Cell A is found to be increased from 9.54% to 10.30% with an enhancement of 8%. The \(J-V\) curves of Cell A with and without the AuNM/ITO integrated film are given in Fig. 5. The \(I-V\) measurements for both cells further confirmed that the efficiency enhancement was mainly due to the \(J_{SC}\) increase. As obtained from the one-sun \(I-V\) measurement, the difference of the \(J_{SC}\) enhancement between Cell A and Cell B is 2%, while the \(V_{OC}\) is almost unchanged. This \(J_{SC}\) difference is smaller than that obtained from the EQE measurement because of the increased sheet resistance of the AuNM/ITO integrated film (868 \(\Omega/\square\)) compared to that of the ITO film (629 \(\Omega/\square\)). It should be noted that the EQE, \(J_{SC}\) and efficiency enhancement have been repeatable on several solar cells under the same condition.
4. Conclusions

In conclusion, we have demonstrated a facile and scalable method of enhancing the light trapping effect of the ITO film integrated with the LB fabricated AuNM on silicon solar cells. The surface roughness of the AuNM/ITO integrated film is four times larger than that of the planar ITO film. The tapered range texturing on the AuNM/ITO integrated film is formed, which leads to enhanced anti-reflection effects. The EQE of the solar cell with the textured AuNM/ITO integrated film is accordingly enhanced over a broadband wavelength range of 400 – 950 nm. Consequently, the photocurrent $J_{SC}$ is increased by 13%, resulting in an 8% efficiency enhancement due to the enhanced optical performance of the solar cell.

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