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The Role of High Work-Function Metallic Nanodots on the Performance of a-Si:H Solar Cells: Offering Ohmic Contact to Light Trapping

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Hydrogenated amorphous silicon (a-Si:H) solar cells have attracted strong attention as an alternative to crystalline silicon cells due to their significantly lower cost in manufacturing.¹ The desired configuration of amorphous silicon-based solar cells is for sunlight to be incident through the p-type hydrogenated amorphous silicon carbide (a-SiC:H), since hole mobilities are lower than electron mobilities in a-Si:H and photogenerated holes then have a shorter distance to move to be collected. Nearly all the light absorption takes place in the intrinsic layer, and the doped regions are kept thin to minimize light absorption since collection is poor or nonexistent from these regions.

The addition of carbon into the p-type a-Si:H results in a slightly wider bandgap, and this p-type a-SiC:H is often called a “window layer”.^{1,2} The wider band gap reduces the absorption in this “dead” p-type layer resulting in a higher short circuit current (J_{SC}) in the device, and in addition, the wider band gap results in higher open circuit voltage (V_{OC}) by increasing the total device built-in potential. A higher carbon content in the window layer is desirable since it increases its band gap. However, there is a limit to the carbon incorporation that can be used because a Schottky barrier exists at the interface between the transparent conducting oxide (TCO) layer (typically n-type ZnO:Al) and the p-type a-SiC:H. This barrier height increases with the carbon content, causing degradation of the fill factor (FF) in the a-Si:H cell.^{2,3} Although a-Si:H solar cell efficiency can be further enhanced by a great deal over the fundamental limit if this barrier problem does not exist, currently de-

ABSTRACT Addition of carbon into p-type “window” layers in hydrogenated amorphous silicon (a-Si:H) solar cells enhances short circuit currents and open circuit voltages by a great deal. However, a-Si:H solar cells with high carbon-doped “window” layers exhibit poor fill factors due to a Schottky barrier-like impedance at the interface between a-SiC:H windows and transparent conducting oxides (TCO), although they show maximized short circuit currents and open circuit voltages. The impedance is caused by an increasing mismatch between the work function of TCO and that of p-type a-SiC:H. Applying ultrathin high-work-function metals at the interface between the two materials results in an effective lowering of the work function mismatch and a consequent ohmic behavior. If the metal layer is sufficiently thin, then it forms nanodots rather than a continuous layer which provides light-scattering effect. We demonstrate 31% efficiency enhancement by using high-work-function materials for engineering the work function at the key interfaces to raise fill factors as well as photocurrents. The use of metallic interface layers in this work is a clear contrast to previous work where attempts were made to enhance the photocurrent using plasmonic metal nanodots on the solar cell surface.

KEYWORDS: metal nanodots · amorphous silicon solar cells · work-function · transparent conducting oxide · plasmonic · light trapping · schottky barrier

veloped TCO does not offer ohmic contacts to p-type a-SiC:H.

In this paper, we present a method to overcome this Schottky barrier interface problem for solar cells with high-carbon content a-SiC:H window layers, resulting in high-efficiency solar cells with high J_{SC} and V_{OC} without sacrificing FF. The method consists of the use of high-work-function metals, such as gold (Au), platinum (Pt), silver (Ag), and palladium (Pd), as interfacial buffers at the a-SiC:H/TCO interface, which minimizes the Schottky barrier and provides instead an ohmic contact to the p-type a-SiC:H window layer. The metal layer is very thin and forms metallic nanodots instead of a continuous film, giving the added benefit of light trapping.⁴ A strong improvement of the FF has been observed even when higher levels of carbon are incorporated into the p-type a-SiC:H window layer.

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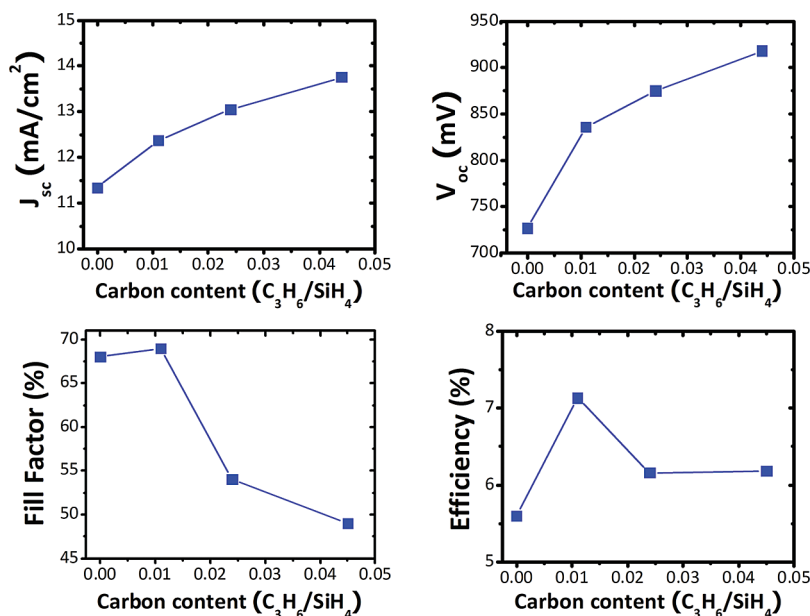


Figure 1. Performance parameters for a-Si:H solar cells without interfacial metal nanodots as a function of the carbon content in the p-type a-SiC:H window.

At the same time, V_{oc} remains high, and J_{sc} is enhanced, resulting in a 31% (relative) efficiency improvement compared to cells without metallic nanodots.

RESULTS AND DISCUSSION

Performance parameters for a-Si:H solar cells without interfacial metal nanodots are shown in Figure 1 as a function of the carbon content in the p-type a-SiC:H window. As other researchers have observed,² both J_{sc} and V_{oc} increase with carbon content, as determined by the propylene (C_3H_6)/silane (SiH_4) ratio. However, the efficiency does not follow the J_{sc} and V_{oc} trend

due to a significant drop of FF at $C_3H_6/SiH_4 > 0.011$. Figure 2a shows the current–voltage behavior for two different carbon contents. The decrease in FF is mostly due to a series resistance (R_s) increase. A series resistance of 6.1 $\Omega\text{-cm}^2$ was measured for the solar cells with $C_3H_6/SiH_4 = 0.011$, while a substantial increase to 50 $\Omega\text{-cm}^2$ was measured for the cell with $C_3H_6/SiH_4 = 0.045$. This internal resistance increase is due to an increase in Schottky barrier behavior at the ZnO:Al/a-SiC:H interface, as indicated by the multiple slopes in the J – V curves of Figure 2a.

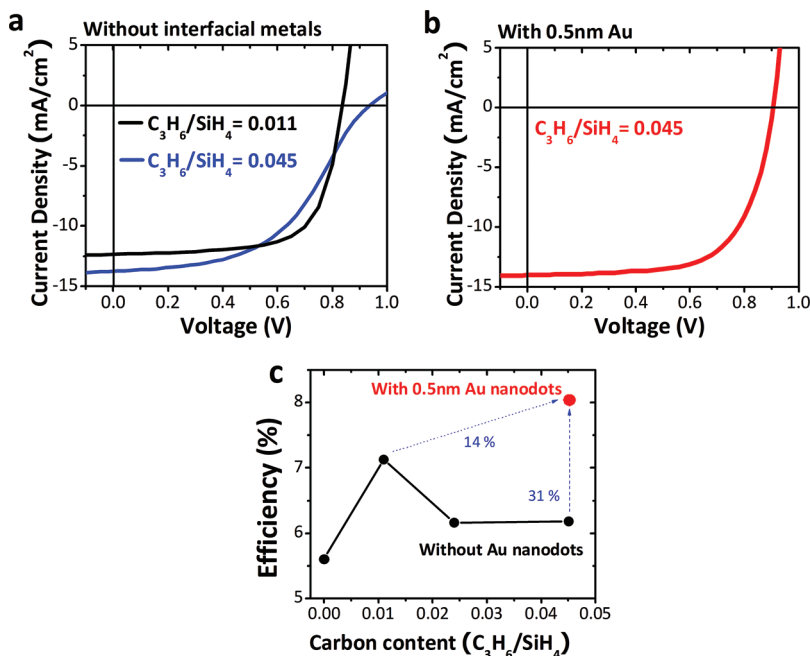


Figure 2. Performances of a-Si:H solar cells with/without metal nanodots. (a) J – V curve for two different carbon contents without metal nanodots, and (b) J – V curve for $C_3H_6/SiH_4 = 0.045$ with metal nanodots. (c) Summary of the efficiency benefits.

This increase in R_s is a fundamental problem caused by the use of n-type TCO layers, such as ZnO:Al, ITO, and SnO₂:F, contacting to p-type a-SiC:H. Since the valence band edge of a-SiC:H is located at ~ 6 eV from the vacuum level while the TCO work function is low (4.35–4.5 eV),^{5–7} the energy band offsets make it impossible to obtain ohmic contacts to p-type a-SiC:H window layers. If p-type TCOs were available, ohmic behavior at the interface might be obtainable. For example, p-type ZnO could result in the desired behavior, but the thermodynamically unstable nature of p-type dopant in ZnO prevents it from being useable.⁸

The FF of these solar cells can be increased or decreased depending on the work function of the thin metal layer deposited at the interface between the window layer and the TCO. We fabricate solar cells with high-work-function (>5 eV) metals at the a-SiC:H/ZnO:Al interface as shown in Figure 3a. Such metals can effectively lower the Schottky barrier height and result in ohmic contacts to the window layer while allowing tunneling current from the metal to the TCO. High-work-function metals (Au, Pt, Pd, and Ag) 2 nm thick were deposited on the ZnO:Al using a thermal evaporator. Solar cells with p-type a-SiC:H windows using C₃H₆/SiH₄ = 0.045, which have a poor FF as shown in Figure 2a, were subsequently fabricated on interfacial metals to determine if the poor FF (= 49%) can be increased. Interestingly, fill factors of more than 60% were obtained and more than 70% for cells with Au interfacial layers (Figure 3b). As shown in Figure 3c, the FF enhancement is mainly due to reduced series resistance.

By contrast, FF values for cells made with interfacial metals, whose work function is lower than ZnO:Al, such as Al and Er, were even less than that without metals, as shown in Figure 3b. Therefore, it is clear that the FFs of a-Si:H solar cells with metal interface buffer layers respond sensitively to the work function of the contact materials made to the p-type a-SiC:H window layer, implying that a Schottky barrier at the window layer/contact interface is truly a limiting factor, particularly when the window layer includes high-carbon content.

Even with such an excellent improvement in the FF, however, the J_{sc} of the cells with 2 nm thick metal interlayers is 10–11 mA/cm², which is lower than J_{sc} (13.7 mA/cm²) of a cell without a metal layer, which must be due to an optical loss caused by the metal. Therefore, thickness optimization is required to determine the conditions that can minimize this optical loss.

Interfacial Au has been chosen for further optimization for high-performance cells, since Au leads to the highest FF enhancement among high-work-function metals and is well-known as a plasmonic material for higher current devices.^{4,9} An enhancement of the J_{sc} of solar cells has been reported by many researchers when plasmonic metals are present at the surface of the cells as scattered nanodots.^{9–11} There exists an optimum density of the nanodots for maximizing surface light

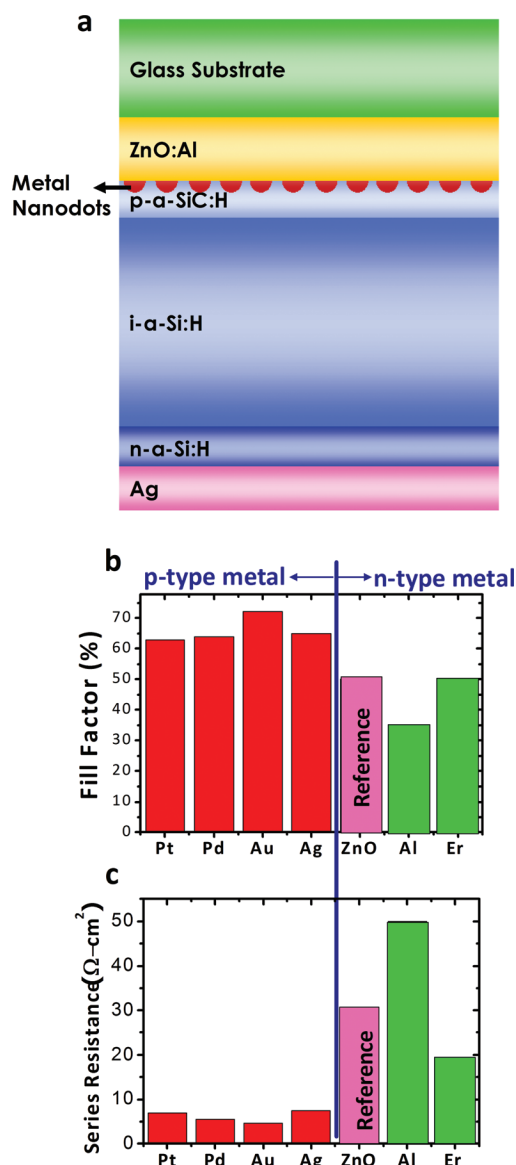


Figure 3. (a) Schematics of a-Si:H solar cell structure using interfacial metal nanodots. (b) Fill factor variation with using different interfacial metal nanodots. (c) Series resistance variation with using different interfacial metal nanodots.

scattering depending on the size of these nanodots. Light-scattering effect is ineffective if the dots are too sparse, while excess reflection/absorption losses result if the dots are too dense.^{10,11} For the conventional use of Au nanodots for J_{sc} enhancement, nanodots are incorporated with a moderate density ($\sim 10^9$ /cm²) in which optical losses are very low.^{9–11} For the work described here, denser Au nanodot arrays are desirable to alter the work function at the ZnO:Al/a-SiC:H interface. Therefore, a trade-off between optical losses from the Au nanodots and the benefits of light trapping must be examined. A continuous Au film would not be acceptable because optical losses would be high and because there would be no benefit of light trapping.

While conventional processes for obtaining arrays of plasmonic nanodots require costly processes, such

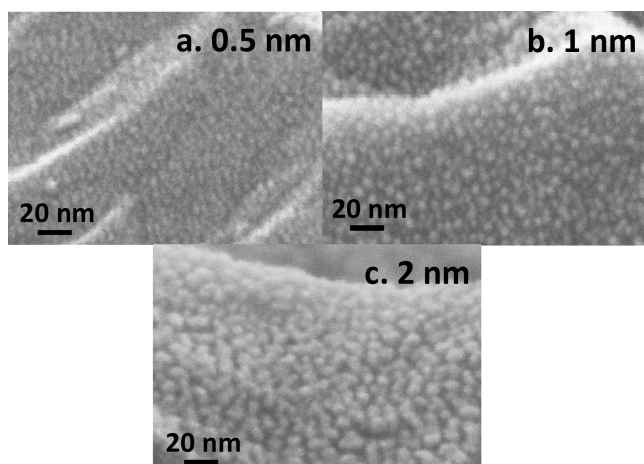


Figure 4. Cross-sectional SEM micrographs of a textured ZnO:Al surface covered with Au nanodots. Au nanodots are shown with aimed growth thickness when Au thermal evaporation is performed. Aimed thicknesses: (a) 0.5, (b) 1, and (c) 2 nm. Average diameters: (a) ~ 3 , (b) ~ 5 , and (c) ~ 8 nm.

as nanoparticle spin-coating and Au deposition through hole patterns, dense arrays of Au nanodots for work-function engineering can be easily obtained by simple evaporation of ultrathin Au films. Since the Au resides at the semiconductor surface with certain wetting angles, Au nanodots are naturally formed when the evaporated layer is not thick enough to form a continuous film. Figure 4a–c shows cross-sectional SEM micrographs of a textured ZnO:Al surface covered with Au nanodots. An increase in the size and the density of the nanodots is observed for increasing thicknesses of the Au evaporation. The figure also shows that the surface coverage is significantly reduced at 1 nm compared to 2 nm.

The parameters for a-Si:H solar cells fabricated with Au nanodots on the surface of ZnO:Al are shown in Figure 5a–d as a function of Au thickness. A monotonic decrease in J_{SC} is observed with increasing Au thickness, as seen in Figure 5a. The linear drop in J_{SC} with increasing Au thickness is related to the linear increase in optical loss at Au. However, a small plateau is seen for 0.5 nm films where the J_{SC} is even higher than obtained in the reference cell without Au. Without the light-trapping effect, this plateau would not exist, and the optical loss due to the absorbing Au film would decrease J_{SC} monotonically for all Au thicknesses. A thickness of 1 nm or less seems to be the critical point where the light-trapping effect becomes dominant over the optical loss. In order to verify this, quantum efficiency (QE) measurements were performed on cells with 0.5, 1, and 2 nm thick Au. Photocurrent enhancement due to plasmonic light trapping can be observed by comparing QE of the solar cells with and without metallic nanodots.¹¹

Figure 5e shows normalized QE obtained by dividing the QE of the solar cells with Au by the QE of the solar cell without Au. The figure shows that the QE of so-

lar cells with 2 nm Au is lower than that without Au throughout the entire wavelength range. On the other hand, the QE of cells with Au less than 1 nm shows enhancement at blue wavelengths and loss at red wavelengths. This experiment shows that 1 nm is a critical thickness for the light-trapping effect to be dominant over the optical loss caused by the Au. It is also consistent with the observation of the Au nanodot morphology discussed earlier, which indicated an abrupt reduction in the density of Au nanodots for evaporated thicknesses less than 1 nm. Moreover, this critical thickness of 1 nm matches the sudden drop in FF as seen in Figure 5b and the increase in V_{OC} seen in Figure 5c as Au thickness reduces. This is another indication for abruptly decreased coverage of Au nanodots below 1 nm from decreasing direct contact area of the p-type a-SiC:H window to ZnO:Al. The monotonic drop in V_{OC} after critical thickness seen in Figure 5c can be attributed to the lower light absorbance. This Au thickness optimization experiment allows us to find the optimum Au thickness of 0.5 nm for the best efficiency, and a substantial efficiency enhancement of $\sim 31\%$ is achieved using the Au nanodots compared to without them. Whether or not the light-trapping phenomena from these small nanoparticles (< 1 nm) is truly related to plasmonic resonance remains to be verified, since such phenomena could be just due to the geometrical enhancement for light scattering.

This process offers a method to improve a-Si:H solar cell efficiency by altering the interfacial property of p-type a-SiC:H/ZnO:Al resulting in strong enhancement in FF at high carbon content in the window layer without sacrificing J_{SC} . A J – V curve of the cells with 0.5 nm Au films is seen in Figure 2b to show substantial enhancement of the cell performance compared to the cells without Au nanodots seen in Figure 2a. The efficiency benefits are summarized in Figure 2c. Compared to the efficiency of the cell with low-carbon content in the p-type a-SiC:H window layer without the Au nanodots, a 14% enhancement is achieved through improvements in J_{SC} and V_{OC} . For high-carbon content, 31% efficiency enhancement is observed for the cells containing 0.5 nm Au nanodots, mostly from enhanced FF and slightly from better J_{SC} .

One thing that should be pointed out is that the use of Au nanodots here is fundamentally different to that of other research groups. Most research focuses on light trapping for solar cells using less dense arrays of Au nanodots on the surfaces of the devices. Here, we employ high densities of Au nanodots internal to the cell structure to allow amorphous Si cells to have p-type a-SiC:H window layers with very high-carbon content. This could be a unique solution to solve the contact problem of ZnO:Al to p-type a-SiC:H window layers, since it is fundamentally difficult to change the work function of ZnO:Al in any other way.

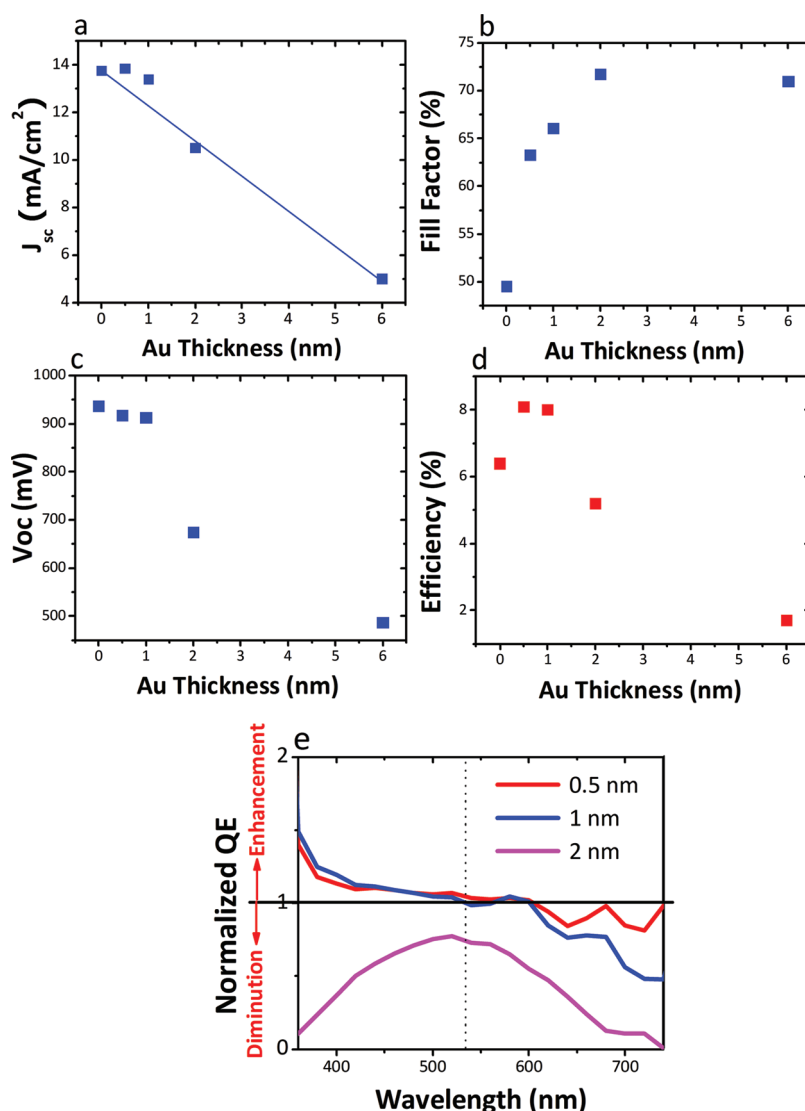


Figure 5. Performance parameters for a-Si:H solar cells fabricated with Au nanodots on the surface of ZnO:Al. (a–d) Photovoltaic parameters as a function of Au thickness. (e) Normalized quantum efficiencies of the solar cells with different Au thicknesses.

CONCLUSION

It has been shown that the nonohmic J – V behavior in amorphous Si solar cells with carbon-doped p-type a-SiC:H window layers is caused by a work function mismatch between the TCO electrode and the window layer. This Schottky barrier-like behavior manifests itself as a monotonically decreasing FF as the carbon content is increased. The addition of a thin, high-work-function metal layer at the interface between these

materials results in a greatly improved work function match at the interface and consequently ohmic behavior, significantly increasing the FF and efficiency. Thin metal layers result in discontinuous films morphologically represented as nanodots which can have the benefit of light trapping. A relative efficiency enhancement of over 30% is obtained by applying Au nanodots at the TCO/a-SiC:H interface in amorphous Si cells with high-carbon content.

METHODS

A borofloat glass was used as the substrate. An 1.5 μ m thick ZnO:Al was deposited on the substrate as a transparent front contact, and the ZnO:Al surface was textured by etching in 1% aqueous HCl solution. A high-work-function metal (Au, Pt, Pd, and Ag) was deposited on the ZnO:Al by thermal evaporation (growth rate = 0.2 nm/s) to a thickness of 0.5–6 nm. The metal layer deposited on the ZnO:Al was kept thin enough to form discontinuous dots with less than

2 nm dimensions. The morphology of the metal film was observed by using SEM. The samples were then loaded into a plasma-enhanced chemical vapor deposition (PECVD) chamber, and p–i–n amorphous Si stacks were deposited with the following parameters: 15 nm p-type a-SiC:H; 320 nm i-a-Si:H; and 15 nm n-type a-SiC:H. Silver was deposited as the bottom contact. The a-SiC:H windows were deposited with different carbon contents by changing the gas ratio between SiH₄ and C₃H₆. Efficiency of the solar cells was measured us-

ing a solar simulator with steady-state illumination for the AM1.5 spectrum, calibrated with a NIST traceable pyrometer.

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