

Degradation of a Thin Ag Layer Induced by Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate in a Transmission Electron Microscopy Specimen of an Inverted Polymer Solar Cell

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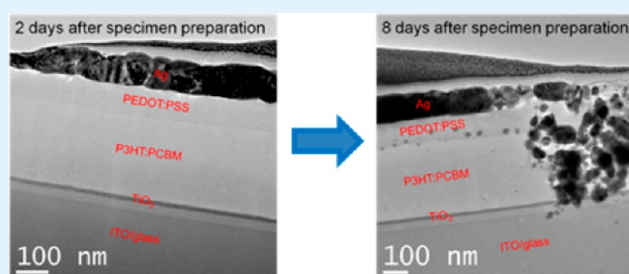
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ABSTRACT: It was found that the Ag electrode layer in a transmission electron microscopy (TEM) specimen of an inverted polymer solar cell structure of Ag/PEDOT:PSS/P3HT:PCBM/TiO₂/ITO/glass (where PEDOT is poly(3,4-ethylenedioxythiophene), PSS is polystyrene sulfonate, and ITO is indium tin oxide) was broken down into particles as time passed. In order to investigate the cause of Ag particle formation and the effect of the degradation on the performance of solar cells, the temporal change of the cross-sectional TEM micrographs was examined together with energy-dispersive X-ray spectroscopy (EDS) analysis and electron tomography. Temporal degradation of Ag/Si and Ag/1 nm-Ti/PEDOT:PSS/ITO/glass structures was also studied. Absorption of water by the PEDOT:PSS layer followed by corrosion of the grain boundaries of the Ag layer by the corrosive water was thought to be the reason of Ag particle formation and fast performance lowering of the device.

KEYWORDS: Ag layer, inverted polymer solar cell, particles, transmission electron microscopy, energy-dispersive X-ray spectroscopy, electron tomography



1. INTRODUCTION

Polymer solar cells (PSCs) are being actively explored worldwide as a promising alternative to silicon solar cells.^{1–4} Besides the low power conversion efficiency smaller than 10%, the short lifetime of PSCs due to degradation is still a major issue to be addressed before PSCs could be widely accepted in the market. There have been several mechanisms proposed for degradation of PSCs: diffusion of oxygen and water into the device; photochemistry and photo-oxidation of polymers; chemical degradation of the indium tin oxide (ITO) electrode or the PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) layer by diffused ions of metal electrode; and chemical degradation of the metal electrode.⁵ It was thought that nanometer-scale observation of the cross-sectional geometries was needed to identify what factors induce degradation of the devices. We set out to investigate what morphological changes occur in the Ag layer. Transmission electron microscopy (TEM) specimens were prepared by focused ion beam (FIB) milling, and we observed temporal change of the structure with TEM focusing on the Ag layer. Electron tomography was also employed to confirm the 3D nature of the particles formed after specimen preparation. The energy-dispersive X-ray spectroscopy (EDS) was also employed to analyze the composition of the particles.

2. EXPERIMENTAL SECTION

Figure 1 shows the geometry of our inverted polymer solar cell. The following procedure was used to manufacture this structure. TiO₂ nanoparticles were dispersed in 1-butanol with a concentration of 0.5 wt % and spin-coated onto the ITO substrate followed by drying at 60 °C for 10 min in a vacuum oven to obtain a 20 nm thick TiO₂ layer. A P3HT and PCBM solution of a weight ratio of 1:0.8 in chlorobenzene

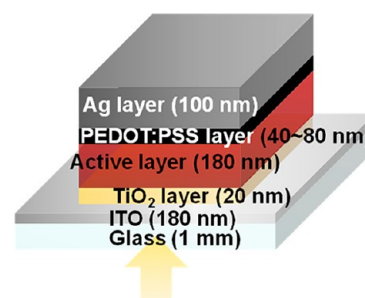


Figure 1. Schematic of an inverted polymer solar cell.

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was spin coated on top of the TiO₂ layer to get a 180 nm thick active layer, and subsequently, the PEDOT:PSS solution was spin-coated onto the active layer and dried at 80 °C for 10 min in a vacuum oven to get a thickness of 55 nm. Finally, a 100 nm thick Ag metal electrode was vacuum deposited. These layers were directly annealed at 135 °C by a radiation heater for 10 min in the same thermal evaporator. Other structures of Ag/Si and Ag/Ti/PEDOT:PSS/ITO/glass were also prepared using similar procedures except that sputtering was used to deposit a 1 nm thick Ti layer for the Ag/Ti/PEDOT:PSS/ITO/glass structure.

Both fresh and degraded inverted PSCs samples were studied by cross-sectional TEM. These samples were prepared as thin TEM specimens by scanning electron microscopy/focused ion beam (SEM/FIB) (FEL, Dual Beam Nova 200 Nanolab) using Ga⁺ ion. 30 kV was used for the main thinning down stage, while the voltage was reduced to 5 kV for the final thinning down stage to minimize damage to the specimen. The samples were observed by TEM (JEOL/JEM-2100F). 3D image reconstruction of degraded metal particles was performed by electron tomography to analyze the shapes and positions of the particles. The composition of the structures of the TEM specimens was analyzed by EDS.

3. RESULTS

Figure 2a shows the cross-sectional TEM micrograph of a fresh inverted PSC sample. A clear interface between the Ag and

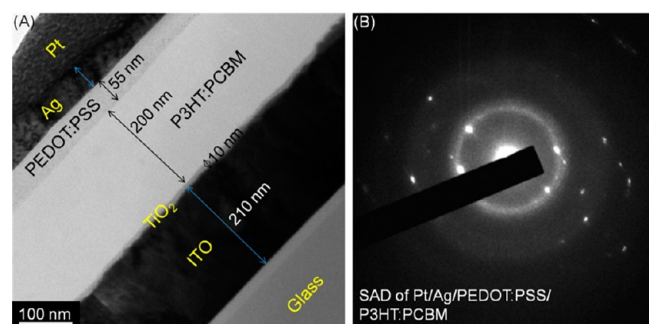


Figure 2. (a) Cross-sectional TEM micrograph and (b) SAD pattern of Pt/Ag/PEDOT:PSS/P3HT:PCBM in an inverted PSC specimen.

PEDOT:PSS layers could be seen, when it was observed immediately after FIB preparation. The SAD pattern shown in Figure 2b consists of diffraction spots from Pt and Ag and the rings from amorphous PEDOT:PSS/P3HT:PCBM.

Figure 3a shows a cross-sectional image of an inverted PSC which had failed after being exposed to direct light. This specimen was observed immediately after FIB preparation. From this picture, we can see that particles with diameter ranging from 2 to 15 nm were formed around the interface between PEDOT:PSS and P3HT:PCBM. Figure 3b shows a magnified TEM image of a particle. This enlarged lattice image shows that this particle is polycrystalline. The measured interplanar spacing of this particle is 2.2 Å, corresponding to the theoretical spacing of Ag₂S. Figure 3c,d shows EDS analysis results of PEDOT:PSS and the particles of this specimen, respectively. From the EDS result, the intensity ratio of silver and sulfur was measured as 1.32. Even though the sulfur peak might have originated partially from P3HT:PCBM as well, this EDS result, in conjunction with the measured interplanar spacing, definitely shows that the particle is a compound of silver and sulfur. We will discuss later in the discussion how silver diffused through the PEDOT:PSS layer to the P3HT:PCBM layer to form these particles. Figure 4 shows the electrical characteristics and performance of an inverted

PSC sample having the structure shown in Figure 1 with a short lifetime. Sudden drops in device performance during operation suggest that somehow degradation seems to be accelerated during light exposure.

Another fresh inverted PSC TEM specimen was analyzed by cross-sectional TEM imaging 3 months after FIB preparation. Particles ranging from 20 to 50 nm in diameter were formed on the PEDOT:PSS layer, as shown in Figure 5a,b. The EDS analysis on a particle in Figure 5c shows that the particles are mainly composed of silver. The Cu peak is from the grid while the C and S peaks are from the PEDOT:PSS layer.

Figure 6 shows the cross-sectional TEM micrograph of the inverted PSC TEM specimen from Figure 5, observed 9 months after FIB preparation. Particles have become a little larger, ranging from 30 to 60 nm in diameter. Now, the Ag layer became so thin that a part of the electrode was disconnected. Figure 7 shows the front and side views of a reconstructed 3D image of this specimen made by the electron tomography method. A series of TEM images at different tilt angles were acquired, and a 3D image was reconstructed by automatic computing routines. From the front view of Figure 7a, we cannot discern whether the Ag particles remain in the layer. However, the side view of Figure 7b clearly shows that most of the particles still remain in the Ag layer, and only a small number of them slipped out of the layer and down through the specimen.

As we have seen above, the Ag layer in the inverted PSC TEM specimen was broken down to Ag particles as time passed. This finding is the first one of this kind in PSCs as far as we know. Therefore, we decided to investigate the degradation of the Ag layer more systematically by studying the change over time in the cross-sectional TEM images of the inverted PSC specimen.

A fresh cross-sectional specimen was first observed 7 h after preparation by FIB, as shown in Figure 8. There are many grain boundaries in the Ag layer, as seen in Figure 8a. A grain boundary is clearly shown at the left of the Ag layer in Figure 8b, which is a magnified micrograph of the region denoted by a dotted rectangle in Figure 8a. We can see that the Ag layer begins to change its morphology, by forming grain boundary grooves. As a result, the Ag layer forms curved interfaces with both the PEDOT:PSS layer and the SiO₂ protection layer.

The TEM micrograph in Figure 9 was obtained from a different region of the same sample 2 days after TEM specimen preparation by FIB. We can see that the Ag layer has interfaces of more rugged and round shapes than the example shown in Figure 8, which was observed 7 h after FIB preparation. Grains are also expected to have round shapes in the vertical direction of the specimen because the upper and lower areas of the specimen are not blocked by any constraint. This morphological change is mainly due to formation of grain boundary grooves at the junctions between grain boundaries and the interfaces (or the air). We can also see grain boundaries being formed at the upper left part of the Ag layer. The size of each grain decreased to approximately 30 to 40 nm in diameter in Figure 9 from approximately 100 nm in diameter in Figure 8.

The TEM micrographs shown in Figure 10 were obtained 8 days after the TEM specimen was prepared. In the region of greater thickness under the thick protection layer shown in the left side of Figure 10a, the Ag layer has still not been divided into particles, while a small number of Ag particles with average diameter of approximately 20 nm were scattered in the PEDOT:PSS layer. A small number of particles appears to be

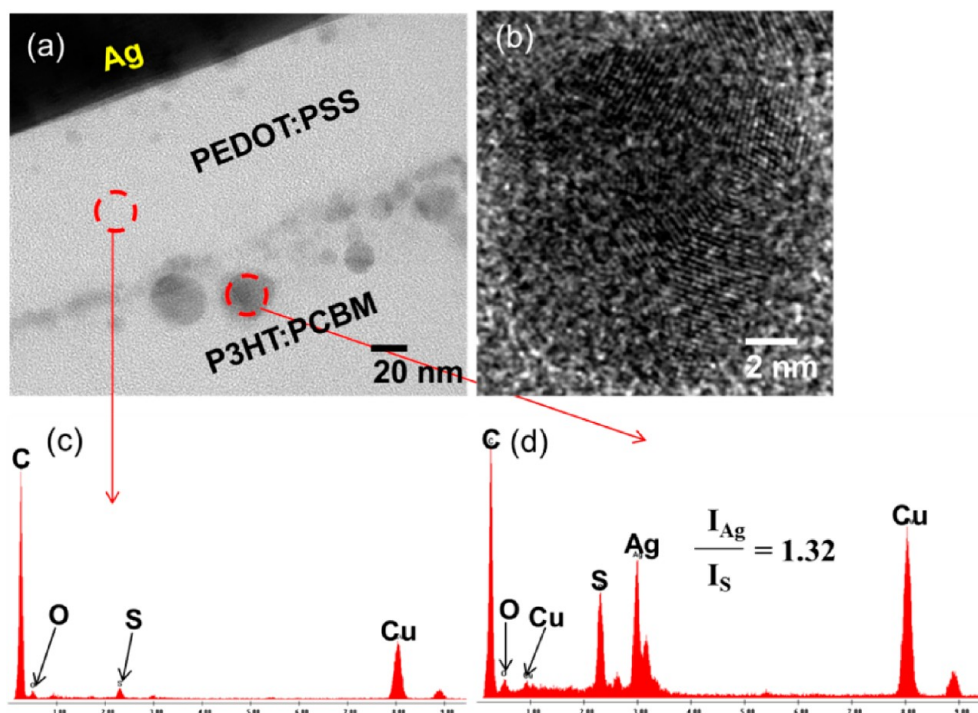


Figure 3. (a) Cross-sectional image of a degraded inverted solar cell sample, (b) enlarged TEM image of a particle in (a), (c) EDS analysis result of the PEDOT:PSS layer, and (d) EDS analysis result of a particle.

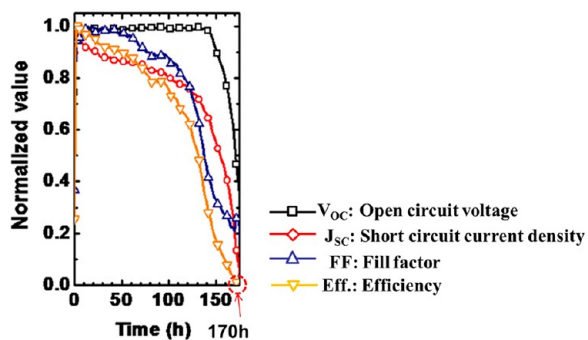


Figure 4. Degradation of electrical performances of an inverted PSC with a durability of 170 h during the reliability test.⁶

diffused into the PEDOT:PSS layer, but the majority came out of the Ag layer and became attached to the surface of the PEDOT:PSS layer. In fact, a large portion of the Ag layer became particles and many of those particles came out of the Ag layer, probably because the layer was so thin that the particles could not be held there.

Figure 11 shows a cross-sectional TEM micrograph of the same inverted PSC specimen whose micrograph was obtained 3 weeks after the specimen was prepared. The micrograph shows that numerous Ag particles are scattered from PEDOT:PSS to the glass substrate.

Finally, we observed the same specimen with TEM 70 days after FIB specimen preparation, as shown in Figure 12. Most Ag particles have left the Ag layer region, which has become nearly vacant.

EDS analysis was performed on the Ag particles, and the result is shown in Figure 13. The oxygen peak and the Ag peak are shown, and the results indicate that the particles were partially oxidized. The Cu peak came from the grid while the C and S peaks are from the PEDOT:PSS layer. There is no Ga

peak observed, indicating that Ga was not implanted into the specimen by the FIB processing while making TEM specimens. Therefore, Ga must not have been involved in any role of breaking down the Ag layer into particles.

In order to obtain some evidence of what plays a key role for particle formation, we examined the temporal change of cross-sectional TEM micrographs of the Ag/Si and Ag/1 nm-Ti/PEDOT:PSS/ITO/glass structures as well and saw whether Ag particles are formed in these specimens as time passed. Figure 14 shows the cross-sectional micrograph of the Ag/Si specimen after 24 and 864 h, and we can see that no particles were formed. By this experiment, we concluded that oxidation of the Ag layer through the reaction with ambient air was not the cause of particle formation. As shown in Figure 15, the Ag/1 nm-Ti/PEDOT:PSS/ITO/glass showed no particles formed 24 h after FIB preparation. However, 312 h after FIB preparation, we can see that some particles were formed, but only in a localized region of the interface between the Ag layer and the PEDOT:PSS layer where Ti may not have been properly deposited, and they were scattered on the PEDOT:PSS layer. From this second supplementary experiment, we could see that a barrier layer like Ti could suppress formation of Ag particles.

4. DISCUSSION

We can summarize the experimental results of Ag particle formation as follows. (1) The phenomenon of Ag particle formation was observed only when there was a PEDOT:PSS layer in the structure. We could not observe formation of Ag particles for the Ag/Si specimen. (2) The thinner the cross sectional width of the specimen, the greater was the particle formation rate. (3) Particle formation was preceded by formation of grain boundary grooves. (4) A 1 nm-Ti layer between the Ag layer and the PEDOT:PSS layer seemed to suppress formation of Ag particles.

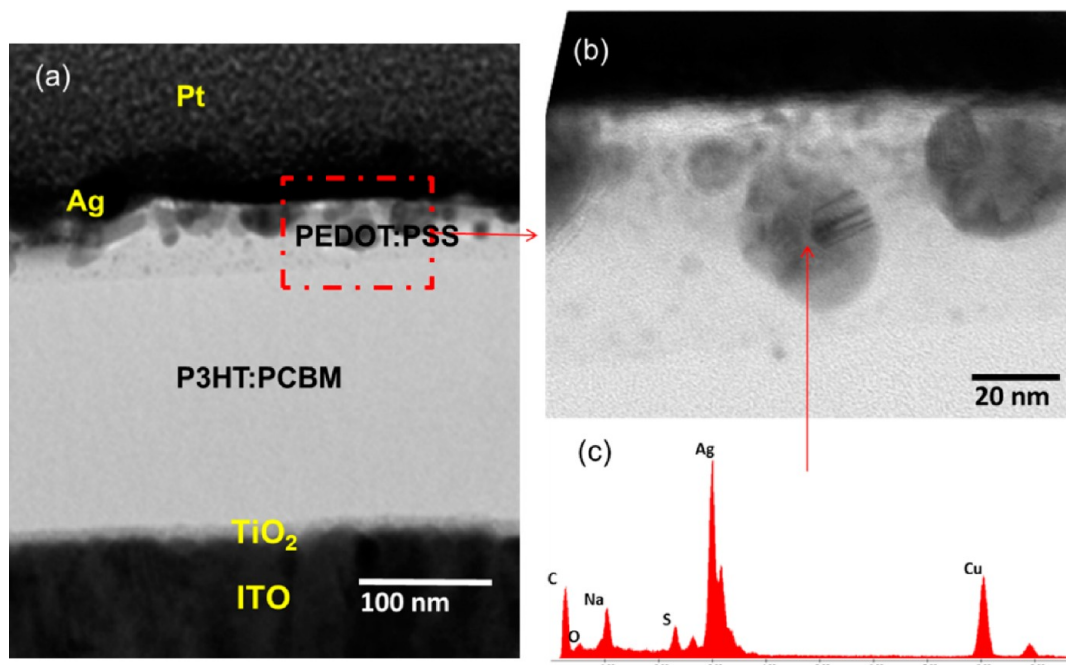


Figure 5. (a) A cross-sectional TEM micrograph of an inverted PSC that was stored under indoor ambient light for 3 months after FIB preparation, (b) a magnified TEM micrograph for the region marked in (a), and (c) EDS analysis result on a particle indicated in (b).⁶

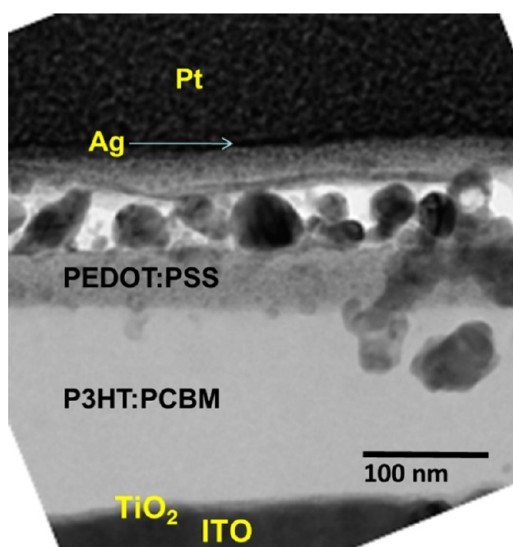


Figure 6. Cross-sectional TEM micrograph of an inverted PSC that was stored under indoor ambient light for 9 months after FIB preparation.

According to this summary, it is clear that PEDOT:PSS plays the most important role for Ag particle formation. Therefore, in order to understand how Ag particles are formed and performance degradation was preceded by the geometry and composition change of the Ag layer, at first, we should discuss the properties of PEDOT:PSS.⁷ PEDOT:PSS is a water-soluble polyelectrolyte, and it has very useful properties such as good film forming properties, high conductivity, and high transparency. However, PEDOT:PSS is acidic (pH \sim 1) and hygroscopic, in other words, absorbs water. Thin layers of PEDOT:PSS films up to a thickness of about 100 nm instantly absorb water from the environment, causing swelling of the films.⁷

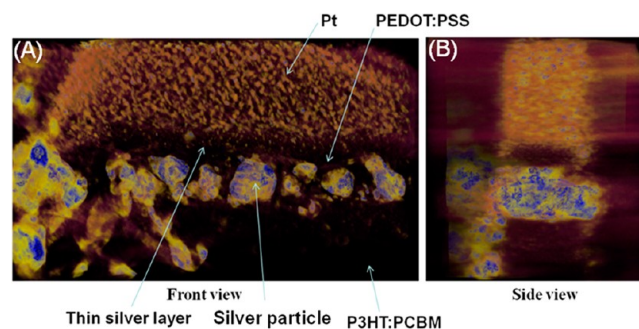


Figure 7. (a) Front view and (b) side view of a reconstructed 3D image of an inverted PSC specimen that was stored under indoor ambient light for 9 months after FIB preparation.

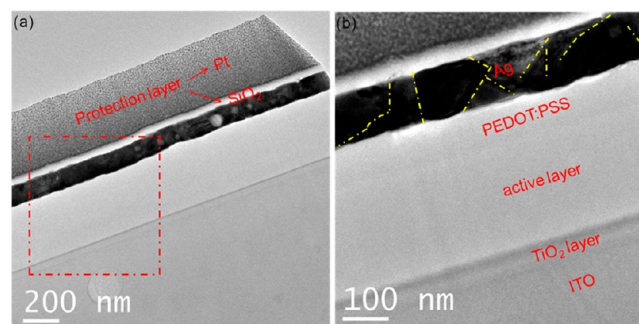


Figure 8. Cross-sectional TEM micrographs of inverted polymer solar cell specimens viewed at (a) low and (b) high magnifications 7 h after specimen preparation.

The acidic and hygroscopic nature of the PEDOT:PSS layer has been blamed for degradation of not just the PEDOT:PSS layer itself but also the ITO electrode in PSCs. According to the study by Aziz et al.,⁸ one of the major causes of degradation of light-emitting diodes (OLEDs) is the inclusion of moisture

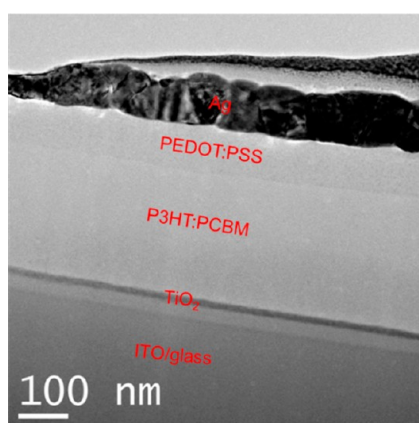


Figure 9. Cross-sectional TEM micrograph of another inverted PSC specimen that was stored in darkness for 2 days after the specimen was prepared by FIB.

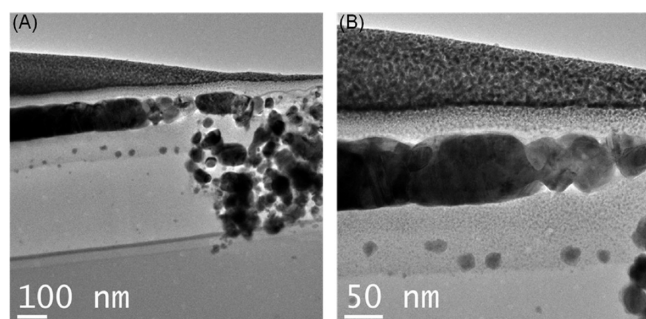


Figure 10. Cross-sectional TEM micrographs of the inverted PSC that was stored in darkness for 8 days after the specimen was prepared by FIB. (a) Low magnification and (b) high magnification of a selected region indicated by the square in (a).

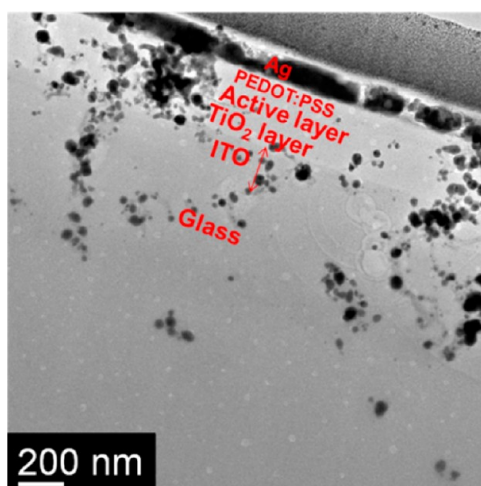


Figure 11. Cross-sectional TEM micrograph of the Ag layer in an inverted PSC specimen that was stored in darkness for 3 weeks after the specimen was prepared.

within the polymer which enhances ionic conduction and hence accelerates corrosion. Jorgensen et al.⁵ reviewed degradation studies of polymer solar cells, and they proposed that the Al electrode transfers electrons to polymer with the creation of anion radicals on the polymer. These anion radicals will react with water molecules introduced in PEDOT:PSS, leading to the loss of conjugation in the polymer. De Jong et al. have studied

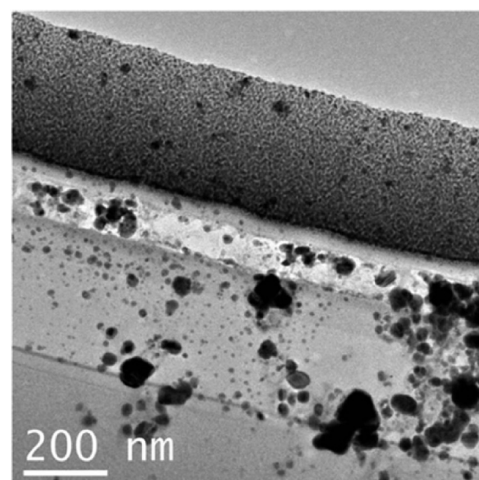


Figure 12. Cross-sectional TEM micrograph of an inverted PSC specimen taken 70 days after FIB preparation.

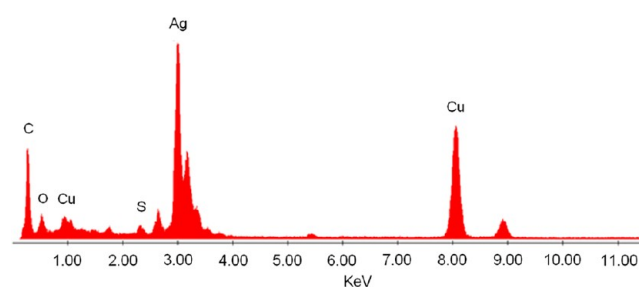


Figure 13. Composition analysis results of the particles.

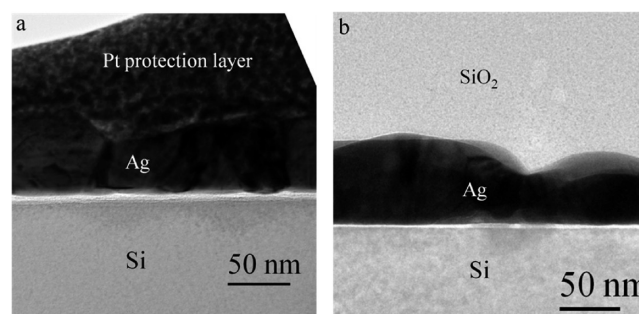


Figure 14. Ag/Si structure (a) 1 day after FIB preparation and (b) 36 days after FIB preparation.

the stability of the interface between indium–tin oxide (ITO) and PEDOT:PSS.⁹ When samples of ITO/PEDOT:PSS were stored in a nitrogen atmosphere at 100 °C for up to 2500 h in the dark, the indium content increased from 0.02% to about 0.22%. However, a film stored at 8 °C in air had 1.2% indium in the PEDOT layer after 10 days. This result indicates that water is easily absorbed by PEDOT:PSS, facilitating corrosion of the ITO layer due to the hygroscopic and acidic nature of PEDOT:PSS.

On the basis of our experimental results and above literature survey on the effect of the hygroscopic and corrosive nature of PEDOT:PSS on polymer solar cells, we concluded the following scenario of how the particles were formed. The PEDOT:PSS layer in our TEM specimen absorbs water very quickly from the ambient atmosphere due to the very small thickness of the TEM specimen. The acidic nature of PEDOT:PSS makes the absorbed water corrosive. This

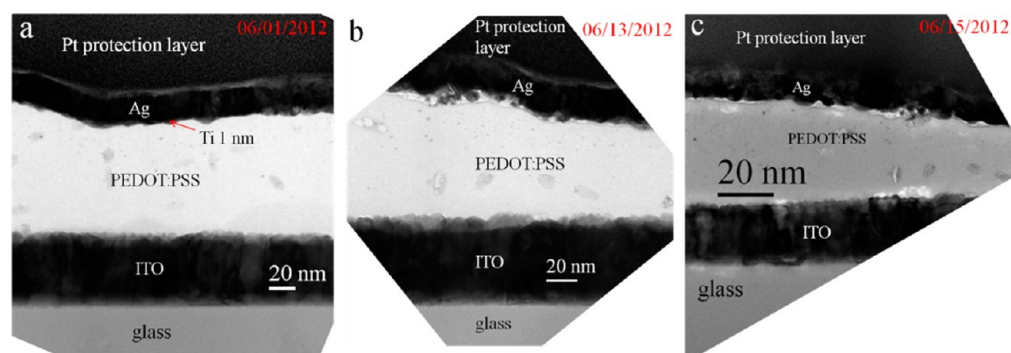


Figure 15. Temporal change of Ag/1 nm-Ti/PEDOT:PSS/ITO/glass structure.

corrosive water then diffuses to the Ag layer and corrodes, especially at the grain boundary junctions, forming grain boundary grooves. We suppose that a thin layer of corrosive water covered on the Ag layer acts also as a medium to move Ag atoms, probably Ag^+ ions, away from the grain boundary junction to other surface regions of the Ag layer. That should be the reason why we could observe relatively accelerated growth of Ag particles at room temperature. Actually, we have observed grain boundary grooves as soon as 7 h after the specimen preparation, and fully shaped grain boundary grooves 2 days after specimen preparation. The diffused acidic water would continue to corrode the grain boundaries, finally separating the grains from each other to form particles. The surface of the grains would be oxidized by the corrosive water during this process which is confirmed by the existence of the oxygen signal in the EDS data of Figure 13. Therefore, the final result of this process is the diffusion of oxygen atoms from the PEDOT:PSS layer to the Ag particles. In the reverse direction, a small amount of Ag would diffuse to the PEDOT:PSS layer like indium diffused to PEDOT:PSS as observed by de Jong et al.⁹ The diffusion of water from PEDOT:PSS to the Ag layer could be enhanced by the rough interface caused by bad interface adhesion between these two different materials. On the other hand, 1 nm thick Ti seemed to be effective in retarding diffusion of corrosive water.

Here, it should be pointed out that there were no particles observed just after TEM specimen preparation, meaning that the above-mentioned phenomenon of particle formation has not occurred at a discernible rate in the bulk structure before it was made into a TEM specimen. This phenomenon was observed only because the specimen we studied was a very thin TEM specimen in which absorption of water by PEDOT:PSS must have proceeded at a much faster rate than by a bulk structure. Therefore, this experiment of observing particle formation on a TEM specimen is an accelerated testing of degradation.

We can explain what has happened to the degraded inverted PSC sample whose cross-sectional TEM micrograph was shown in Figure 3, in terms of the above scenario as well. The inverted PSC sample in a bulk state might also have absorbed a very little amount of water which diffused to and corroded the Ag layer slightly. Ag^+ ions formed during the process might have diffused through the PEDOT:PSS layer to the interface between the PEDOT:PSS and P3HT:PCBM layers and reacted with sulfur atoms in the polymers by help of direct light to form Ag_2S particles. That could be the reason why we found Ag_2S particles in this sample when observed even just after FIB preparation.

In a real device, absorption of water would be too slow to show any degradation of the Ag electrode in a short period of time. However, in a very long period of time, either absorption of water during the operation of the device or inclusion of water during device processing by PEDOT:PSS followed by degradation of the Ag electrode might become the main cause of degradation of the device. To prevent formation of Ag particles and subsequent PSC failure, a proper encapsulation of PSCs should be implemented, preventing water absorption into the device. As another option, we may need to replace PEDOT:PSS as the hole injection layer with other materials like V_2O_5 .¹⁰ A layer that retards diffusion of water between the Ag and PEDOT:PSS would be also effective in prolonging the lifetime of PSCs.

5. CONCLUSIONS

Ag particles were formed as time passed from the Ag layer in a TEM specimen of Ag/PEDOT:PSS/P3HT:PCBM/TiO₂/ITO/glass. From the EDS analysis result where there was no Ga peak observed, it was concluded that Ga was not involved in forming Ag particles from the layer. It was also concluded from the result of no particle formation for the Ag/Si TEM specimen that oxidation of the Ag layer through the reaction with the ambient air was not the cause of Ag particle formation. Absorption of water by the PEDOT:PSS layer followed by corrosion of the grain boundaries of the Ag layer by the corrosive water was thought to be the reason of Ag particle formation. The grain boundary grooving was suggested as an evidence of the fast progress of corrosion through grain boundaries. A 1 nm Ti layer placed between the Ag and PEDOT:PSS layers seemed to retard formation of Ag particles. In conclusion, a tight control of water incorporation into devices and a proper encapsulation of devices should be implemented in order to reduce the degradation of PSCs. A layer like Ti that retards diffusion of water between the Ag and the PEDOT:PSS layer may be needed for increasing the lifetime of PSCs.

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Notes

The authors declare no competing financial interest.

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