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Silver nanoparticles cause snail trails in photovoltaic modules

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ABSTRACT

After some months of operation, a number of PV modules develop a discolouration defect called "snail trails", or "snail traces", which appear as irregular dark stripes across the cells. Whereas these traces were soon identified as discoloured silver contacts along the cell edges or at micro cracks, the chemical and mechanistic reasons for this phenomenon have not yet been resolved in detail. In this work we show that silver nanoparticles accumulating within the encapsulation foil cause the brownish discolouration, and that certain additives of encapsulation and back sheet foils trigger the formation of these nanoparticles.

1. Introduction

The investigation of defects and degradation in photovoltaic modules has become an important subject since reliability and product lifetime are key to system performance and to conditions of warranty. One of the degradation effects that has been observed increasingly during recent years is "snail trails", thus called because of their visual appearance. They occur a certain period (several months to several years) after initial installation and appear as discolourations on the cell edges and intersecting dark lines. Snail trails are a widespread phenomenon affecting modules from more than 13 manufacturers worldwide [1]. They have been found on modules with mono-crystalline silicon cells as well as on those with poly-crystalline silicon. Despite manifold concerns of customers, as yet there is no indication that they cause a significant decrease in module efficiency [2]. However, longer-term negative influences cannot be excluded and require further study.

It could be shown previously that the visible dark lines are regions with discoloured contact fingers on the cell surface, occurring either at the cell edges and/or at micro cracks [3,4]. This observation is strong evidence that moisture is a key factor in snail trail formation: Since back sheet foils show certain water vapour permeability, moisture from the environment can enter the module from the back and reach the cell surface by diffusion through the encapsulation foil only at the cell edges or at micro cracks. This belief is corroborated by the observation that the formation of snail trails seems to be inhibited by the additional moisture protection at the position of the junction box (Fig. 1).

The main goal of the work presented here is to uncover the chemical and microstructural nature of discoloured grid fingers. We investigated thoroughly several PV modules affected by snail trails after outdoor exposure, as well as mini modules with snail trails induced after treatment in the damp-heat chamber. We can show that the same chemical mechanism is underlying the grid finger discolouration in both the real modules and the model system. This enables us to set up a model for the formation of snail trails and to develop strategies for their prevention.

2. Material and methods

PV modules with snail trails were disassembled mechanically to obtain the cell and encapsulation foil surface. Optical microscopy (Olympus SZX 16) was used to study discoloured grid fingers before and after module disassembly. Cross-sections from grid fingers and encapsulation foil were prepared for transmission electron microscopy (TEM, FEI Tecnai F20) by a focused ion beam (FIB Zeiss AURIGA Laser). Energy dispersive X-ray spectroscopy (EDS, SDD Apollo from EDAX) was applied for elemental analysis of the nanoparticles. In addition, the chemical fingerprint of the discoloured foil samples was analysed using time-of-flight secondary ion mass spectroscopy (ToF-SIMS, Iontof V).

Samples of different encapsulation foils about 3×3 cm^2 in size were incubated for 24 h before and after cross-linking in 0.1 M or

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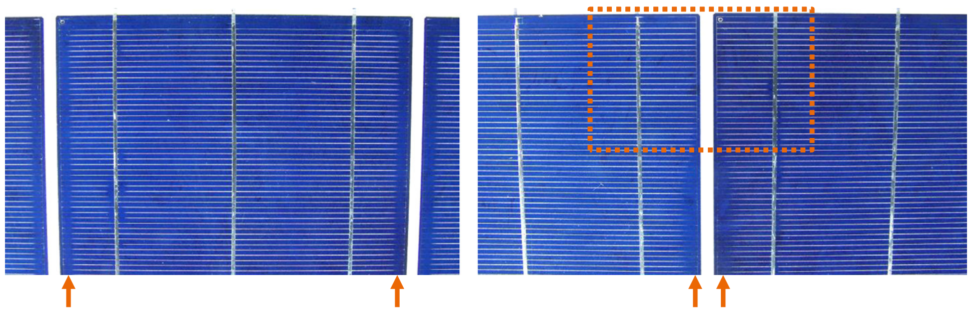

Fig. 1. Photograph of cells with snail trails at the edges (left) and of the same module at the position of the junction box marked with an frame (right). Only at the junction box are the bright lines of the grid fingers visible to the very edge of the cell (the arrows are eye guides to the grid finger discoloration at the solar cell edge).

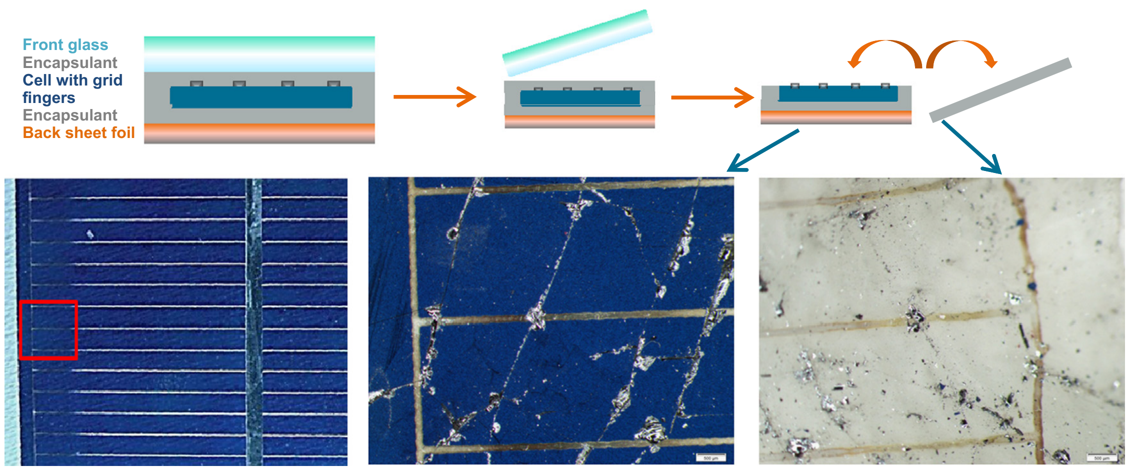

Fig. 2. Top: Schematic illustration of sample preparation. Bottom: Microscopic images of a sample with snail trails at the cell edge (left), cell surface after foil removal (middle), cell side of the lifted encapsulant (right). The red square marks the zoomed area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1 M aqueous $AgNO_3$ solution at 40 °C. The foil samples were documented in photographs. UV–Vis Spectroscopy measurements were carried out using a Varian Cary 300 (Mulgrave, VIC, Australia) spectrometer. For both the measurement and the baseline correction, a calibrated reflectance standard in 8° geometry was used.

Fourier transform infrared (FTIR) investigations of EVA foils were performed using transmission mode in a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with a deuterated-triglycine-sulfate detector with potassium bromide window (DTGS KBr).

X-ray photoelectron spectroscopy measurements were done by XPS spectrometer Sage 100 (Specs Surface nano Analysis GmbH). Al-*K*a irradiation was used at a pressure of 10 − 7 mbar in Constant Analyser Energy mode.

3. Results and discussion

3.1. The discolouration is located close to the interface between the cell and encapsulation foil

After localisation of typically discoloured grid fingers, a module exhibiting snail trails was dismounted and prepared for microstructural and chemical analysis. Fig. 2 schematically shows the preparation process and the results. After removal of the front glass and the back sheet foil, the front layer of the encapsulant was lifted off the cell surface. The microscopic image of both sides of the cell-encapsulation foil interface revealed that the brownish discolouration is located mainly within the encapsulation foil at the sites of the grid fingers (Fig. 2, bottom raw).

From this finding, it became clear that not only the contact fingers themselves were discoloured. Rather, the encapsulation foil directly adjacent to the silver contact has brownish lines displaying the contact finger pattern.

3.2. A high density of particles containing Ag causes the brown colour

To discover the origin of the discolouration the samples shown in Fig. 2 were used to prepare cross-sections (perpendicular to the surface of the grid finger) by FIB and then imaged with TEM. The results are the following (Fig. 3): At the surface of the grid fingers and in the encapsulation foil, nm-sized particles were found. The particles within the encapsulation foil TEM sample (thickness about 100 nm) had an area density of 2–4 particles/μm^2. Samples from unaffected sites of the module were prepared and studied by TEM in the same manner and found to be free of particles (data not shown).

Moreover, we investigated the particles in the foil sample by TEM/EDS and found that the particle consists mainly of Ag and, that the polymer matrix (carbon) is reduced at the location of the particle. Furthermore, locally increased intensities for P and S were found with high spatial correlation to the nanoparticle (Fig. 4).

3.3. Snail trails can be induced in the damp-heat chamber

For a systematic study of the reaction conditions necessary for the formation of snail trails, we developed a suitable lab procedure based on mini modules as described in Ref. [5]. Using this procedure we tested various combinations of encapsulation and back sheet foils for their susceptibility or resistance to snail trails.