Research Article

Migration of Sn and Pb from Solder Ribbon onto Ag Fingers in Field-Aged Silicon Photovoltaic Modules

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We investigated the migration of Sn and Pb onto the Ag fingers of crystalline Si solar cells in photovoltaic modules aged in field for 6 years. Layers of Sn and Pb were found on the Ag fingers down to the edge of the solar cells. This phenomenon is not observed in a standard acceleration test condition for PV modules. In contrast to the acceleration test conditions, field aging subjects the PV modules to solar irradiation and moisture condensation at the interface between the solar cells and the encapsulant. The solder ribbon releases Sn and Pb via repeated galvanic corrosion and the Sn and Pb precipitate on Ag fingers due to the light-induced plating under solar irradiation.

1. Introduction

Investigations of the degradation of photovoltaic (PV) modules have been widely performed under various conditions to provide the insights for enhancing the reliability and durability of PV modules [1–4]. Accelerated stress tests become increasingly important for PV modules to ensure the reliability for over 25 years. To identify the degradation or failure modes of PV modules, damp heat (DH) tests are commonly performed under a variety of conditions in a test chamber. DH studies of moisture ingress through the back sheet as a key factor of degradation have given rise to equations describing relative humidity inside the PV module, which is permitting more accurate modelling of water vapor transmission rate and finite element method. To improve further the accuracy of DH tests for the prediction of PV module performance, tests have been performed under various climates [5, 6]. However, the results of these studies are not always consistent in terms of the effects of long-term field exposure. Furthermore, most studies of

field-aged degradation have focused on the phenomenon itself and statistics, rather than clarifying the causes of the degradation. In this paper, we studied the electrochemical reaction between the SnPb solder and the Ag fingers of crystalline Si (c-Si) solar cells that had been field-aged for 6 years. Layers of Sn and Pb were found on the Ag fingers down to the edge of the solar cells whereas they were not seen in the samples tested under the standard DH conditions. DH tests differ from the field exposure in that the samples are not under solar irradiation. The Sn and Pb layers are the result of the migration and the deposition of the elements from the solder ribbon due to the repeated galvanic corrosion and the light-induced plating. The implication of this finding for the reliability of PV modules is discussed in this study.

2. Experimental Procedure

Silicon solar cell samples were taken from the PV modules installed in 2008 at Chilgok (longitude 128°47', latitude 36°03') located in the southeast of the Korean Peninsula.

FIGURE 1: Field-aged PV module sample (a), (b); Chilgok solar power plant sample (c); and (d) degradation area for analysis.

FIGURE 2: SEM image of Sn and Pb precipitation on the Ag finger. (a) Area indicates EDS mapping imaged in Figure 3; (b) FIB area imaged in Figure 4.

This site experienced an average ambient temperature of 13.6°C and an average relative humidity of 64% in 2013. A PV module was constructed of 3.2 mm thick low-iron tempered glass, an ethylene vinyl acetate (EVA) sheet, tedlar-polyester-tedlar backsheet, and 72 series connected mono-Si 5 inch solar cells (EGM-170, Eging). The manufacturer characteristics of a PV module at a light intensity of 1 sun were approximately as follows: open-circuit voltage (V_{oc}): 44.0 V; short-circuit current (I_{sc}): 5.15 A; and maximum power: 170 W. The delamination of encapsulant was observed along the solder ribbon and the Ag electrode of the solar cells. Discoloration of the encapsulant was also observed. Solar cell samples were separated from the PV module using 6 cm diameter diamond round drill as shown in Figure 1(d).

Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a FEI Model Quanta 250 FEG. Sample cross sections were obtained by focused ion beam (FIB).

3. Results and Discussion

3.1. Precipitation of Sn and Pb on Ag Fingers of Si Solar Cells. A mixture layer of Sn and Pb was observed on the Ag fingers at the edge of the solar cells. The top region in SEM image of Figure 2 is the Ag finger electrode originally deposited by screen printing method, while the bottom region is a new layer with a considerable thickness.

FIGURE 3: EDS mapping of area in Figure 2(a).

FIGURE 4: Cross-sectional SEM image of Sn, Pb layer.

Figure 3 shows the result of EDS mapping in area of Figure 2(a); new layer consist of Sn, Pb, and O. Figure 4 shows the cross-sectional images of the Ag finger of the area in Figure 2(b) using FIB. Compared to morphology of SnPb after soldering, phase boundaries of Sn and Pb are ambiguous and porous. The Ag finger was covered with a layer of Sn and Pb with several micrometers thick. The EDS mapping image shows a uniform distribution of Sn and Pb on the bulk Ag finger region, indicating that the glass frit in the Ag layer was not the source of Sn and Pb deposition on the Ag finger. Unlike the initial composition of SnPb solder, the concentration of Pb was higher than Sn in the deposited layer from the result of EDS line scan (Figure 5). As the reaction progresses, the larger amount of solder under the Cu ribbon would be consumed. The thickness of Sn and Pb layer can be locally changed depending on the differences in

the conditions that may cause corrosion, such as delamination and moisture condensation.

3.2. An Assumption for Explaining the Sn, Pb Precipitation Phenomenon. In order to explain the reaction between SnPb solder and the Ag finger, we assumed that there had been a moisture condensation at the interface between the front surface of the solar cell and the encapsulant.

Delamination of the solar cell and EVA is a common phenomenon observed in the field-aged PV modules. Precipitation of impurities, such as sodium, phosphorous, and tin, weakens the adhesional shear strength of the cell/EVA interface [7]. The delamination usually takes place along the solder ribbon and the Ag fingers, due probably to the stress associated with the height difference between the solder ribbon and the surface of the solar cell. In addition, a high

FIGURE 5: EDS line scan area and results.

strain exists at the corners of the solder ribbon and the solar cell, due to differences in the thermal expansion coefficients [8–11]. Moisture condensation at the interface should occur under certain conditions, typically at dawn, when the temperature goes below the dew point. Water droplets should easily form in the PV modules when the moisture condensation condition is combined with the delamination of the cell/EVA [12].

3.3. Migration and Precipitation of Sn and Pb by Galvanic Corrosion and Light-Induced Plating. The reaction related to the formation of Sn and Pb layer on the Ag fingers consists of four steps as follows (Figure 6):

- Moisture condensation at the cell/EVA interface.
- Dissolution of the SnPb solder (anode) in the moisture by galvanic corrosion and migration of the cations in the moisture:

Anode (SnPb):

Cathode (Ag):

- Light-induced plating (LIP): transport of electrons to Ag fingers under solar irradiation, reduction of Sn and Pb cations, and the precipitation of Sn and Pb metal on the Ag surface:

Cathode: front side (Ag):

Anode: rear side (SnPb):

- Repeated occurrence of steps (a)–(c) yields the extensive dissolution of the solder ribbon and the deposition of Sn and Pb on Ag fingers upon a long-term field exposure.

FIGURE 6: Schematic of mechanism by the Sn and Pb layers formed on the Ag finger.

When water condenses at the region near the SnPb solder and the Ag finger, the SnPb (acting as the anode) ionizes in the water droplets (acting as the electrolyte) because of the difference in the standard electrode potential between Ag (0.800 V), Sn (−0.136 V), and Pb (−0.126 V) [13]. The electrode potential difference causes electrons to flow towards the Ag grid by galvanic reaction, typically at dawn when the extent of moisture condensation is the largest. Galvanic corrosion rate depends on the potential difference between the dissimilar coupled metals, geometric factors such as the ratio of contact area in the electrolyte, and the electrolyte properties such as pH, conductivity, and impurity. According to the standard electrode potentials, Sn should be ionized more readily than Pb. However, the relative electrical potential of Sn and Pb may change depending on the characteristics of the electrolyte [14]. The corrosion rate also depends on the pH of the electrolyte solution, which may change due to the presence of acetic acid generated by the decomposition of EVA. The electrolyte would be composed mainly of the water and acetic acid generated from EVA. It should be noted that hydrogen gas would form as a result of the galvanic corrosion. The hydrogen gas evolution could be one of the reasons for the bubbles often observed in the back sheet of the field-aged PV modules [7]. Under solar irradiation, Ag fingers are expected to serve as the cathode for Sn and Pb metal ion plating. The photogenerated electrons are collected on the Ag fingers and chemically reduce the Sn and Pb cations in the electrolyte, which precipitate as a solid metal. The anodic reaction should occur in the rear side of the solar cell because of the photogenerated holes. The candidate metals for the anodic reaction should be Al in the back contact and SnPb alloy in the solder ribbon on the back busbar. Al should not dissolve as readily as SnPb alloy due to the dense oxide layer usually found on the Al surface [13]. In step (c), light-induced plating, rear SnPb could be oxidized to counterbalance for front reduction reaction. Moreover,

rear SnPb is more vulnerable because of moisture ingress through the backsheet. Cu inside PV ribbon appears by severe oxidation of rear SnPb as shown in Figure 7. Therefore, the anodic reactions in the rear side of the cells should follow the equations given above. As the reaction repeats, the precipitation area of Sn and Pb expands to the edge of the solar cell. PV modules that are exposed for several years can suffer from moisture and delamination and can be degraded by the phenomena that promote galvanic corrosion and LIP of SnPb solder.

4. Conclusion

We investigated the phenomenon of Sn and Pb precipitation from solder on the front Ag fingers in 6-year field-aged PV modules. The three key factors underlying this phenomenon are the presence of moisture condensation, ionization of the SnPb solder to cations (Sn^{2+} , Pb^{2+}), and sunlight irradiation. Exposure of the PV modules under UV, high temperature, and daily thermal cycles causes the interfacial adhesion between the front EVA and the cell to degrade and creates voids, due to delamination at the interface between nearby PV ribbon and Ag grid. The penetration of moisture through the breathable backsheet under long-term exposure can lead to moisture condensation when the cell is cooled below saturation limit during the night. The potential difference between the two solder metals, Sn and Pb, caused their ionization by galvanic corrosion. The subsequent reduction of Sn and Pb cations, by photo-generated electrons under irradiation in the daytime, causes the precipitation of Sn and Pb metal on the front Ag fingers of the cell. In summary, the precipitated layer of Sn and Pb on the Ag grid, upon long-term field exposure of PV modules, occurs via corrosive oxidation of the SnPb solder and subsequent reduction of the Sn and Pb cations. The cell performance by the series and contact resistance is less degraded. However, delamination and cracking of the solder

FIGURE 7: SEM images and EDS analysis on surface of SnPb before/after degradation.

bonds can accelerate the degradation of PV module. Reducing the amount of solder, precipitation can affect the series resistance of cell.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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