DAMP HEAT STABILITY OF TRANSPARENT CONDUCTIVE ZINC OXIDES: ROLE OF ENCAPSULANTS AND PROTECTIVE LAYERS

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ABSTRACT: The mechanisms and environmental influences that cause photovoltaic modules performance degradation are poorly understood, but it is well known that water vapour is deeply implicated in the degradation process. Indeed, some layers and interfaces of thin film modules can be moisture sensitive and depending on the processing conditions, they degrade after exposure to damp heat conditions (85°C, 85% relative humidity) [1]. Transparent conductive oxides (TCO), as used in CIGS or thin silicon film cells play a particular role linked to reliability issues. We showed recently that low-pressure chemical vapour deposition zinc oxide (LPCVD ZnO) can withstand damp heat test even without encapsulant providing doping of the ZnO is high enough, though this is unfavourable for free carrier absorption (reduction of spectral response in the infrared part) [2]. Reduction of doping leads to improved optical properties but needs therefore an optimized encapsulation strategy to avoid the deterioration of the TCO conductivity.

In previous work, the degradation of LPCVD ZnO used in thin-film silicon solar cells was investigated [3]. It was shown that the decrease of the ZnO conductivity was essentially due to the humidity increasing inside the encapsulant. However other effects take part in the degradation process and remained yet unexplained.

In this paper we will report on several other possible sources of degradation, which have been identified. In order to demonstrate and quantify these effects, we used various encapsulants, but without back protection (foil or glass), and we exposed the samples to different type of atmospheres. The resistivity of the ZnO was monitored using an inductive contactless and a four points probe methods. Finally, schemes to perform highly reliable laminates when using lightly doped ZnO are proposed.

Keywords: conductivity, degradation, moisture, zinc oxide

1 INTRODUCTION

In the field, thin-film PV modules are subjected to various detrimental factors, such as heat, water vapour and oxygen. Depending on the encapsulation system, as the polymers are more or less permeable, the sensitive layers (TCO) might be exposed to atmospheric gases or chemicals coming from the encapsulation polymers.

ZnO layers are commonly used as sensors for gas such as oxygen, acetone and hydrocarbons [4]. Depending on the ZnO layer characteristics (thickness, deposition process) its resistivity can change when exposed to the mentioned gases which might get chemisorbed, by trapping electrons, and reduce their conductivity, or react with chemisorbed species which give back electrons.

Here we evaluate the protection that various inorganic or polymeric layers can bring to the ZnO layer, by monitoring its conductivity against time of degradation. The results can be of practical importance for all modules incorporating ZnO, including CIGS and thin film silicon.

2 EXPERIMENTAL

2.1 Sample design

Glasses of 41*41mm^2, 0.5mm thick, were coated with Low Pressure Chemical Vapour Deposition Zinc Oxide (**Figure 1** a), boron-doped (2 doping level: Low Doping LD and Medium Doping MD). Some ZnO layers were then coated with silicon oxide or nitride (**Figure 1** b), by Plasma Enhanced Chemical Vapour Deposition at 200°C. Some of the ZnO substrates, without (**Figure 1** c) and with (**Figure 1** d) SiO_x and SiN_x layers, were coated with commercial PV white reflective ink applied by manual screen printing (mesh 25µm) and dried in an oven. The others were encapsulated with two different polymers, A and B, in a R&D vacuum laminator S1815 from 3S. Polymer A was commercial ethylene vinyl acetate (EVA) and polymer B was another ethylene copolymer, both designed for photovoltaics purpose.

All the ZnO layers were ultra-sonic soldered at their 4 corners.

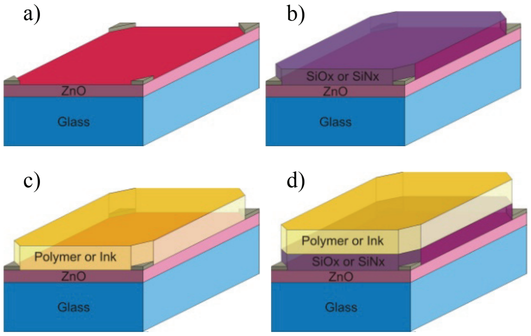

Figure 1: Sample types. Soldering: in grey.

This design differs from usual photovoltaic panel encapsulation by the lack of back-foil or glass. In this way, the degradation of the ZnO occurs much faster.

2.2 Aging

In order to differentiate the influences of temperature, atmosphere and encapsulant, the samples described above were separated into four sets which were aged under different conditions:

- Argon at room temperature
- Argon at 85°C
- Oxygen at 85°C
- Air at 85°C and 85% Relative Humidity

The three first sets were placed in desiccators, which were purged once with argon and then filled with the above mentioned gas (600mbar at 25°C), and stored at room temperature or placed in an oven at 85°C. A Dycometal climate chamber, set at 85°C and 85%RH, was used to age the last set of samples.

2.3 Measurements

A Wafer Lifetime Tester from Sinton Consulting [4] was used to measure the sheet resistance inductively. Due to the detection limit above 100 Ohm square, those measurements were completed with four points probe measurements. They were performed with a source-meter Keithley 2612, in four wires resistivity measurement mode (current = 1mA).

3 RESULTS

3.1 Visual

After 400h, for all studied configurations, no degradation was observed, except for the polymer B which became orange in presence of oxygen at 85°C.

3.2 Comparison with module encapsulation

The samples described in 2.1 differ from a normal module encapsulation because there is no back-sheet or back-glass to protect the polymer or the ink from direct penetration of water vapour. On the **Figure 3**, the variation of conductivity of a medium doping ZnO encapsulated with a polymer and a back-glass (see **Figure 2**) is much slower than the variation of the samples studied here. (Data from [3]).

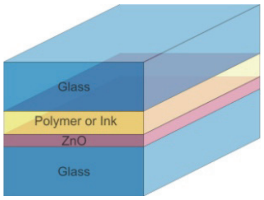

Figure 2: Type e.

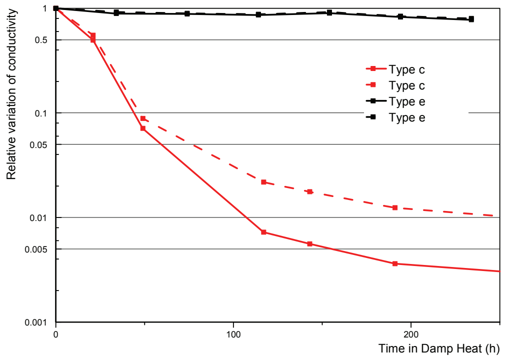

Figure 3: Comparison of the relative decrease of conductivity for ZnO protected by only a polymer (type c) or by a polymer and a back-foil or glass (type e).

3.3 Conductivity measurements

The silicon oxide and silicon nitride layers clearly have a protective effect when deposited on top of zinc oxide layers. On **Figure 4**, after 300h at 85°C and 85%RH, the resistivity of the coated ZnO was at the half value of resistivity as compared to the non-coated ZnO.

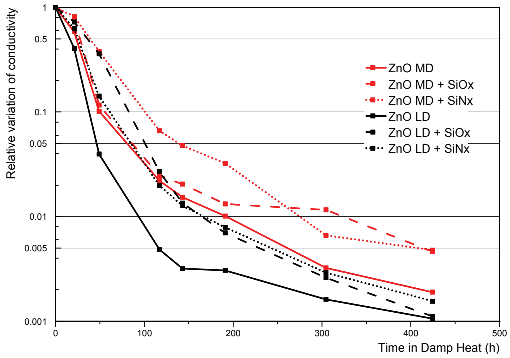

Figure 4: Relative variation of the conductivity of zinc oxide layer, at low doping (LD) and medium doping (MD), without (type a) or with (type b) inorganic layers SiO_x or SiN_x, during aging in climate chamber.

On **Figure 5** and **Figure 6**, we can see that the polymer A has a low barrier effect as compared to the polymer B or to the ink. However, when associated with SiO_x or SiN_x, the protection performances of polymer A become much better than for the 2 others. This effect is similar for the two levels of doping.

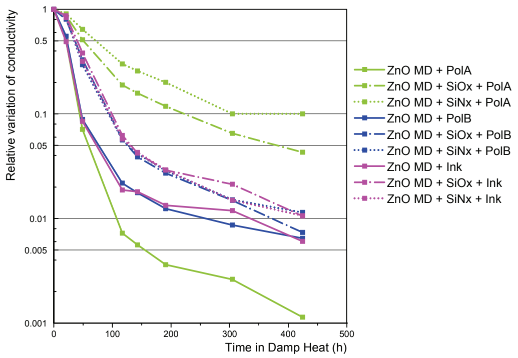

Figure 5: Comparison of the evolution of the conductivity of ZnO MD when encapsulated or coated with ink (type c, plain curves) and the same with or without SiO_x or SiN_x (type d, dashed and doted curves).

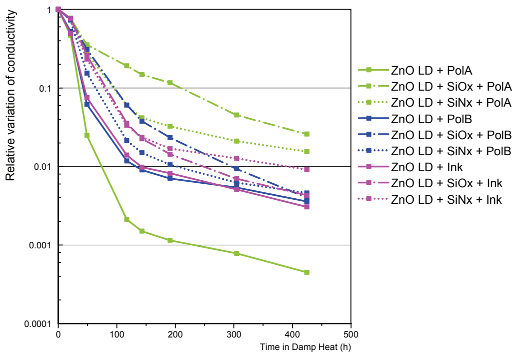

Figure 6: Comparison of the evolution of the conductivity of ZnO LD when encapsulated or coated with ink (type c, plain curves) and the same with or without SiO_x or SiN_x (type d, dashed and doted curves).

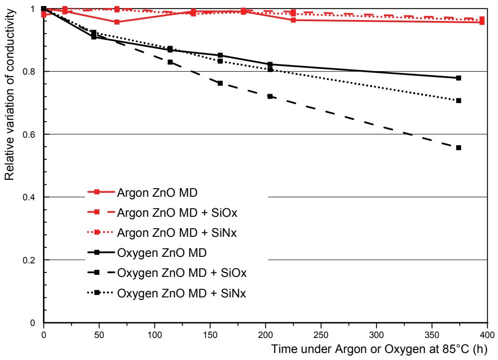

Figure 7: Relative decrease of the conductivity of medium doped ZnO, when exposed to argon (red) or oxygen (black) at 85°C.

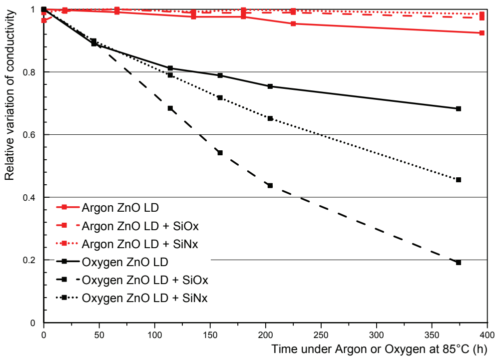

Figure 8: Relative decrease of the conductivity of low doped ZnO when exposed to argon (red) or oxygen (black) at 85°C.

When looking at **Figure 7** and **Figure 8**, one can see that zinc oxide exposed to an inert gas was not much affected by heat, whereas in presence of oxygen the conductivity decreases drastically. This effect was more important for the low doped ZnO. In this experiment, the presence of the SiO_x or SiN_x layers was not favourable at all, the SiO_x giving the worst results.

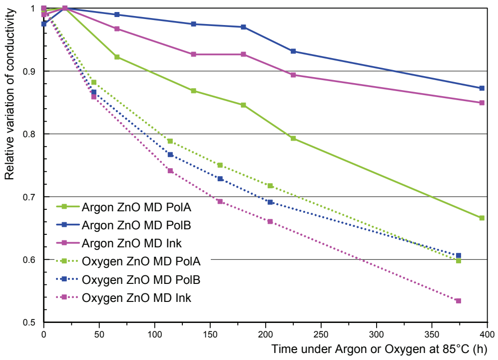

Figure 9: Relative decrease of conductivity of samples encapsulated with Ethylene Vinyl Acetate (green), and exposed to argon or oxygen at 85°C, compared to samples encapsulated with polymer B (blue) or coated with ink (pink).

The variation of conductivity of samples exposed to argon at 85°C remained very stable after 200h (variation of less than 15% of initial value, which means a resistivity variation of less than 2 Ω_{sq}), except for EVA samples were the variation is above 33% (which corresponds to a resistivity increase of more than 5 Ω_{sq}). Nevertheless, for the EVA sample exposed to oxygen, the resistivity increase remains in the same order of magnitude (from 5 to 6 Ω_{sq}), while for the polymer B and the ink the conductivity variation was higher than for EVA.

4 DISCUSSION

We showed here that the deposition of inorganic dielectric layers on the zinc oxide back contact could greatly improve its lifetime, in damp heat chamber (85°C and 85%RH). No clear difference between silicon oxide and nitride effect was detected.

When associated to polymer or white reflective dielectric ink, this effect of the SiO_x or SiN_x is also present. An interesting phenomenon occurred for EVA. Indeed, EVA alone is the worst candidate for ZnO protection, but when associated with SiO_x or SiN_x, its protection effect is much better than with polymer B or Ink associated to SiO_x or SiN_x.

When looking at the decrease of the conductivity of the EVA samples exposed to argon and oxygen and the above mentioned phenomenon, it seems clear that more than just oxygen or water vapour permeation occurs. The decrease of the conductivity of the EVA samples under argon at 85°C seems to indicate that chemicals evolve from EVA at this temperature which are detrimental to ZnO. Isolating the polymer from the ZnO with a SiO_x or SiN_x layer prevents those volatiles or degradation by-products to reach the ZnO surface.

5 CONCLUSION

The polymer plays an important role on the lifetime of the thin film silicon modules. From this study we conclude that the gases permeation is not the only important criterion to select a polymer. It is crucial to identify the chemical composition and the by-products coming from the polymer degradation as they probably are directly involved in the ZnO layers degradation. Finally it is interesting to see that a thin dielectric layer can act as a protective coating. Therefore it might not be compulsory to use high performance polymers, which are much more expansive.

6 REFERENCES

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