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Inert drying system for copper paste application in PV

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Abstract

In this study we show that the electrical characteristics of low temperature polymer pastes are improved by carrying out the curing process in an inert nitrogen atmosphere. In order to reduce the solar cell production costs, numerous scientific works are devoted to the question, whether the commonly used silver paste can be replaced by a copper based paste. However, a major problem with the latter is, that copper tends to oxidate during the thermal treatment. Hence, this work focuses on the development of an inert inline drying system to avoid the oxidation of copper based polymer pastes. For reference, silver based polymer pastes are investigated simultaneously. Therefore the influence of different nitrogen curing atmospheres on the electrical resistance and the weight loss of the pastes is evaluated. The electrical resistance of both silver and copper based pastes is improved by reducing the residual oxygen concentration. To investigate the reason for this, the samples are analyzed by micrographics. Furthermore it is shown, that the weight loss of the pastes shows no dependence on the curing atmosphere.

Keywords: Low temperature metallization; polymer paste; copper; inert drying; nitrogen curing atmosphere; heterojunction cell

1. Introduction

The application of heterojunction solar cells has become common in the field of solar cell research and development due to their high efficiencies and their simple low-cost production process. One reason for such high efficiencies is the excellent passivation quality of a thin layer of intrinsic amorphous Si. Due to the temperature sensitivity of this intrinsic layer the curing process is limited to low temperatures. Hence,

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low temperature metallization pastes and processes have to be further developed. In the work presented here, the curing behavior of conventional available low temperature polymer pastes is analyzed.

In contrast to the commercial used glass containing thick film pastes, the polymer pastes are glass-free consisting basically of polymer and conductive metal particles. At curing temperatures below 200 °C the polymer matrix starts to shrink, so that due to the resulting compression of the metal particles electrical conductive paths arise. The electrical conductivity is still lower than the one of the sintered glass containing thick film pastes (8…10 mΩ/sq). However, as we show in this work, the electrical conductivity of polymer pastes is improved by inert curing conditions and reaches comparable values.

Moreover, the attention regarding copper paste applications for front side metallization grows obviously in the PV market. One simple reason for this progress is given by the approximately 120-times higher price for silver than for copper. However, the replacement of silver by copper causes problems. Besides the challenges in the solar cell process itself, e.g. diffusion barrier, new drying systems are necessary which guarantee an inert atmosphere to avoid the copper oxidation. The latter is important because copper oxide is not electrically conductive. In an earlier work [1] we showed already that an inert curing atmosphere improves the electrical resistance of copper as well as silver based polymer pastes.

To continuously improve the application of low temperature polymer pastes, more knowledge about the influence of the inert curing atmosphere on the electrical and mechanical paste characteristics is necessary. Therefore, this work focuses on analyzing this fact especially on copper based paste, but also on silver based paste for reference. Furthermore, the weight loss of the paste during the curing process and the residual oxygen concentration of the curing atmosphere are evaluated. All these results will provide the basis information for the development of an inert inline drying system.

2. Experimental

2.1. Polymer pastes

Within this work, three different commercial available low temperature polymer pastes are analyzed: one copper paste, one silver coated copper paste and for reference one silver based paste. In Table 1 an overview of their curing condition and electrical characteristics is shown.

Table 1. Overview of polymer pastes

Paste Type	Conductive Particles	Resistance R (*mΩ/sq*)	Curing Profile (°C / min)
1	Copper	20…30	160 / 30
2	Silver coated Copper	65…75	170 / 30
3	Silver	< 22	150 / 30

All pastes were screen-printed on Al_2O_3 substrates and subsequently cured in an inert inline drying system (see section 2.2). In order to investigate the curing behavior of these pastes, different curing profiles and curing atmospheres were tested.

2.2. Inert curing

Both, the screen printing process and the subsequent curing process in an inert inline drying system, took place at Rehm Thermal Systems in Blaubeuren-Seißen. The samples were produced on an existing inline reflow soldering system, which provided the possibility to test various nitrogen atmospheres. The heat transfer was realized exclusively by convection.

The achievable residual oxygen concentration was far below 100 ppm and was measured by a zirconium oxide cell. The samples were cured under three different inert atmospheres: high, medium and low nitrogen. High Nitrogen means a low residual oxygen concentration and a low nitrogen atmosphere is consequently given at a high residual oxygen concentration. As reference process the samples were also cured under ambient atmosphere (air).

Besides the curing atmosphere, the curing profile itself was varied. Therefore it was optimized regarding the electrical conductivity and the paste adhesion on the Al_2O_3 substrates.

Furthermore, the weight loss of each paste during the drying process was analyzed.

2.3. Paste characterization

The investigation of the electrical and mechanical paste characteristics was carried out at the Fraunhofer-Institut IKTS in Dresden. The measurement routine included the characterization of the electrical resistance, coating thickness, adhesion on the substrate and solderability [1].

The electrical sheet resistance R was examined by using a four point resistance measurement method. In combination with the results of the coating thickness measurement, the normed sheet resistance R_{25} was calculated (referred to 25 µm thickness).

To demonstrate the adhesion of the paste on the Al_2O_3 substrates a scotch tape test under an angle of 90° was performed.

3. Results and discussion

3.1. Variation of curing atmosphere

To check whether an inert nitrogen curing atmosphere is beneficial or not, a direct comparison between an ambient atmosphere and a medium nitrogen atmosphere for each paste was performed. All samples were cured under the same drying profile. The results are summarized in Figure 1.

On the left side, Figure 1a shows that the resistance R_{25} of both the copper as well as the silver paste is improved by the nitrogen atmosphere. The resistance of the copper paste is reduced by over 16 % and the resistance of the silver paste indicates an 11 % reduction. On the right side, Figure 1b demonstrates that the silver coated copper paste indicates the strongest dependence on the curing atmosphere by providing a resistance reduction of 54 %. This demonstrates that an inert nitrogen atmosphere leads to an improvement of the electrical resistance of the tested polymer pastes. This statement applies not only as expected to the copper paste, but surprisingly also to the silver based paste.

Besides the electrical resistance the weight loss of the cured paste was analyzed. The results show that there is no obvious correlation between the drying atmosphere and the reduction of weight, for all tested pastes. This finding is presented in Figure 2.

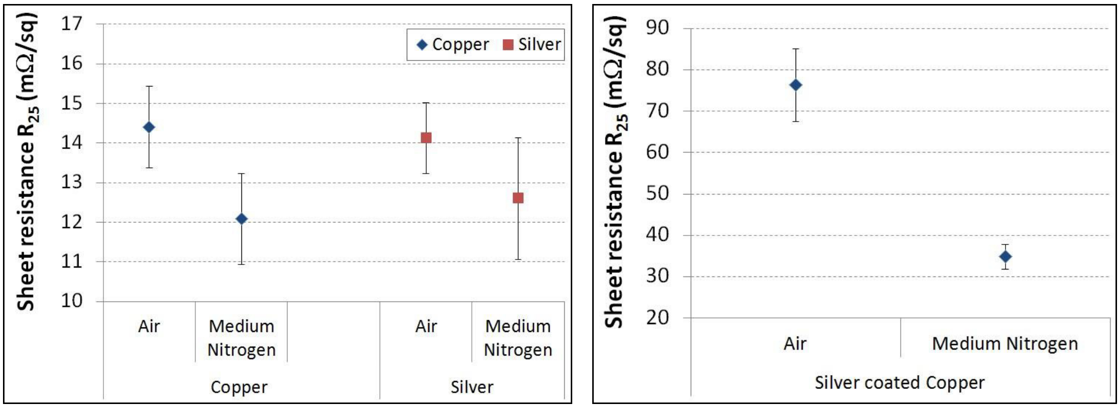

Fig. 1. Influence of ambient atmosphere (air) and medium nitrogen atmosphere on the electrical resistance
(a) Copper and silver paste; (b) Silver coated copper paste

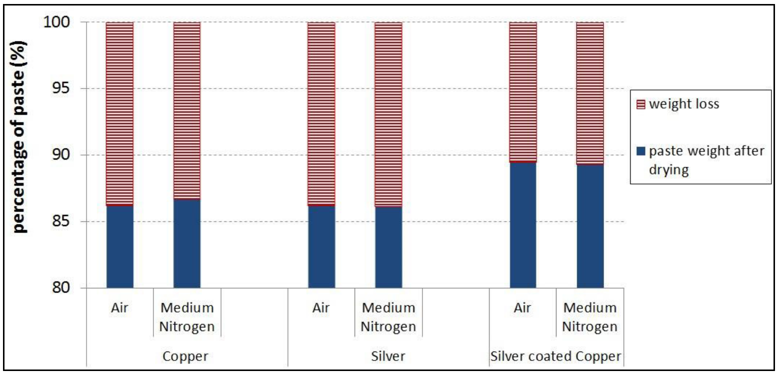

Fig. 2. Correlation between weight loss and curing atmosphere

Additional experiments are necessary to clarify, if a decrease of the residual oxygen concentration will lead to a further reduction of the resistance. Therefore the samples are cured under three different inert atmospheres: high, medium and low nitrogen. By means of these nitrogen variations the correlation between the curing atmosphere and the electrical resistance shows an obvious trend. In Figure 3a the silver coated copper paste indicates, that with decreasing residual oxygen concentration the electrical resistance is reduced. Moreover, especially the silver paste shows a resistance reduction of 49 % by increasing the nitrogen concentration from medium to high. This important result is illustrated in Figure 3b.

In order to investigate the reason for this dependence the samples of the silver paste are analyzed by micrographics. The micrographics are shown in Figure 4 (left: low nitrogen; right: high nitrogen). It seems likely that the agglomeration of metal particles increases with decreasing residual oxygen concentration of the curing atmosphere. This might be explained by the shrinking process of the polymer matrix (polymerization). One possible explanation therefore could be that oxygen harms the linking process of the polymer chains and thus also the polymerization. If less oxygen is available, the polymerization is intensified and the agglomeration of the metal particles increases. Thus, a high nitrogen curing atmosphere will lead to an improved electrical resistance of the polymer paste.

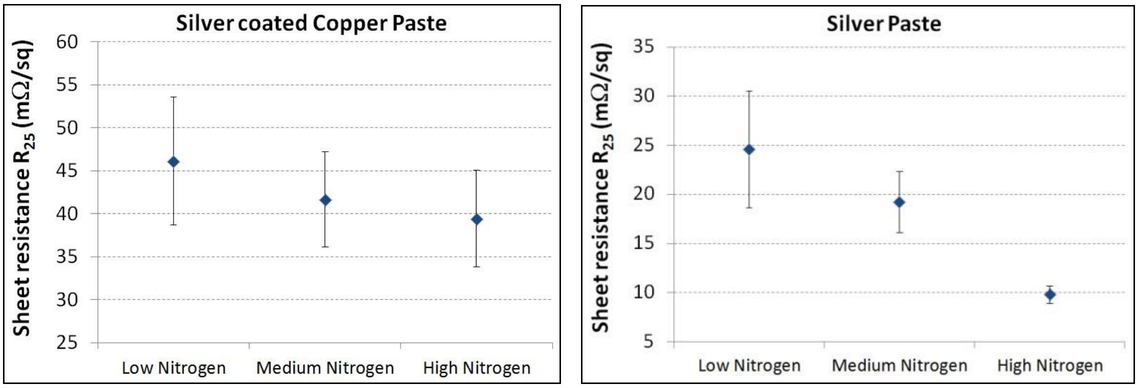

Fig. 3. Nitrogen variations of curing atmosphere
(a) Silver coated copper paste; (b) Silver paste

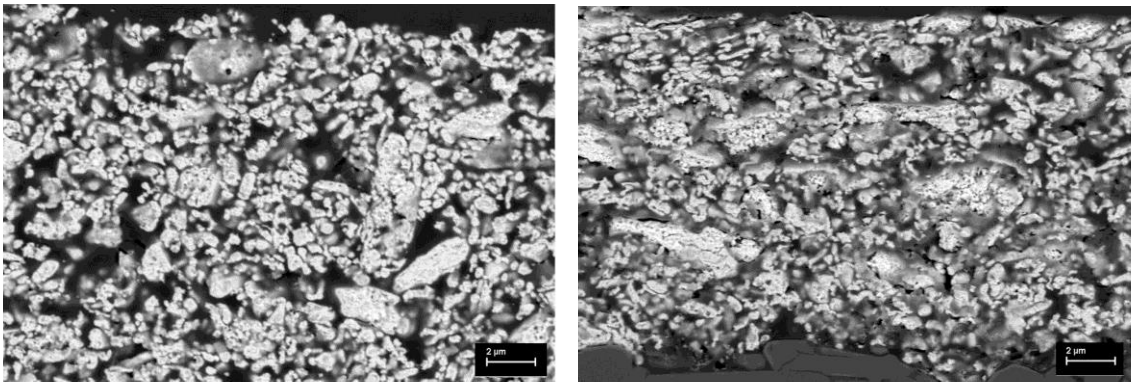

Fig. 4. Micrographics of silver paste
(a) Low nitrogen; (b) High nitrogen

3.2. Variation of curing profile

In this experimental run the curing profile of the copper paste was varied. The curing temperature and the curing atmosphere remained equal, only the process time was changed. The aim was to investigate, whether there exits an optimum curing profile with regard to the paste characteristics or not. In consequence important information for the development of an innovative inert drying system can be achieved, for instance the required oven length.

Figure 5 represents the achieved paste resistances as a function of the varied process time. The continuous line at a resistance of 20 mΩ/sq illustrates the initial resistance based on Table 1. On the top of the graph the results of the adhesion measurement are given. With increasing processing time the adhesion is improved. With respect to both, the electrical resistance and the adhesion, an optimized profile is determined and encircled in Figure 5.

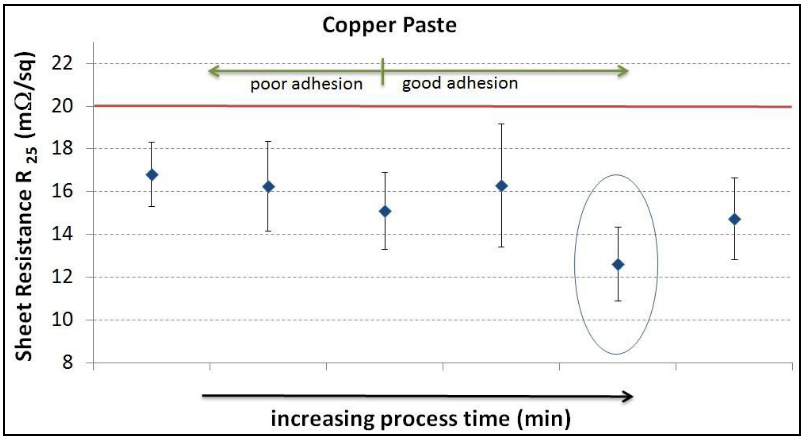

Fig. 5. Variation of curing profile – Copper paste

3.3. Residual oxygen concentration measurements

In addition to the knowledge about the influence of inert curing atmospheres on the paste characteristics, it is important to investigate the real atmospheric condition in the oven itself. For this purpose residual oxygen concentration measurements were performed. These measurements took place in a pilot inert drying system of Rehm Thermal Systems. Contrary to the previous drying system the heat is transferred by infrared radiation. Figure 6 shows the measured residual oxygen concentration of each oven zone. Three to four measurements were done per zone. The continuous line at 100 Vol.ppm represents the limit of the residual oxygen concentration concerning the nitrogen settings of the oven. The resulting oven profile is visualized by the dotted line and calculated by the mean value of each zone. Thus, this measurement demonstrates that a stable inert nitrogen atmosphere below 100 ppm is achievable in an inert inline drying system.

Moreover, first comparable samples were produced on both drying systems, on the previous convective reflow system and on the pilot infrared drying system, in order to obtain information about the influence of the heat transfer on the paste characteristics. The resistance of the copper and silver coated copper polymer paste shows no obvious difference between the infrared and the convective heat transfer.

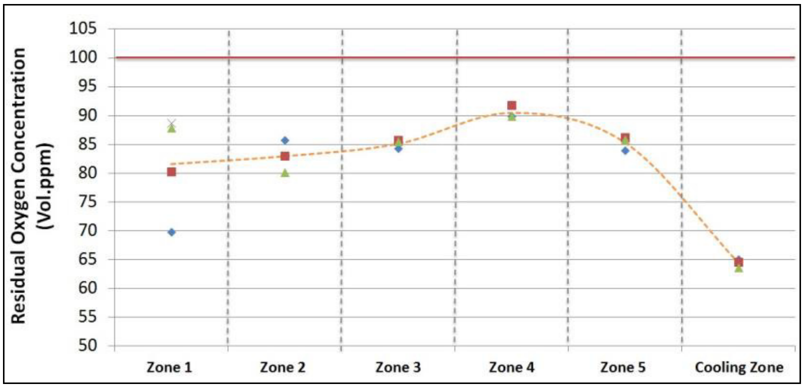

Fig. 6. Profile of the residual oxygen concentration

4. Summary and conclusion

By means of nitrogen variations of the curing atmosphere, it is shown that a decreasing residual oxygen concentration leads to a reduction of the electrical resistance of the tested polymer pastes. Furthermore, not only the resistance of the copper polymer paste but also the resistance of the silver based pastes is improved by a nitrogen curing atmosphere. The reason might be given by a strengthened polymerization and a thereby intensified agglomeration of the metal particles by less residual oxygen concentration. On the contrary, the weight loss of the polymer pastes shows no obvious dependence on the curing atmosphere.

Moreover, due to variations of the process time an optimized curing profile of the copper polymer paste in regard to the resistance and adhesion has been determined. This includes important informations for the development of an inert drying system.

To control the inert curing atmosphere residual oxygen concentration measurements were performed. Thereby it was shown, that a stable nitrogen atmosphere below 100 ppm is possible.

First measurements demonstrate that curing processes with convective and infrared heat transfer achieve comparable results concerning the electrical resistance. Further experiments are necessary to come to a decision whether the convective or infrared heat transfer is more profitable for the application of low temperature polymer pastes.

Within this work all pastes were cured on Al_2O_3 substrates, in a next step the curing behavior of these polymer pastes will be analyzed on solar cells [2].

Acknowledgements

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