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# Conductive Copper Paste for Crystalline Silicon Solar Cells

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Sang Hee Lee and Soo Hong Lee

Additional information is available at the end of the chapter

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## Abstract

In photovoltaic industries, the main technique of metallization is screen printing with silver pastes due to its simple and quick process. However, the expensive price of silver paste is one of the barriers to the production of low-cost solar cells. Therefore, the most focused target in photovoltaic research is the decreasing consumption of silver paste or substitute silver for other materials. As a proper candidate, copper has been researched by many institutes and companies since it has a similar conductivity with silver even though the price is inexpensive. To apply copper as a contact for solar cells, the plating technique has been actively researched. However, copper paste, which was mainly developed for integrated circuit applications, has been recently researched. Mostly, copper paste was developed for the low-temperature annealing process since copper tends to oxidize easily. On the other hand, firing type copper paste was also developed by coating copper particles with a barrier layer. This chapter discusses recent development of copper paste for the application of solar cells and its appropriate annealing conditions for better electrical properties. Also, the light I-V characteristics of copper paste on the solar cells in other research papers are summarized as well.

**Keywords:** copper paste, oxidation barrier coating, curing, silicon heterojunction solar cells, passivated busbar

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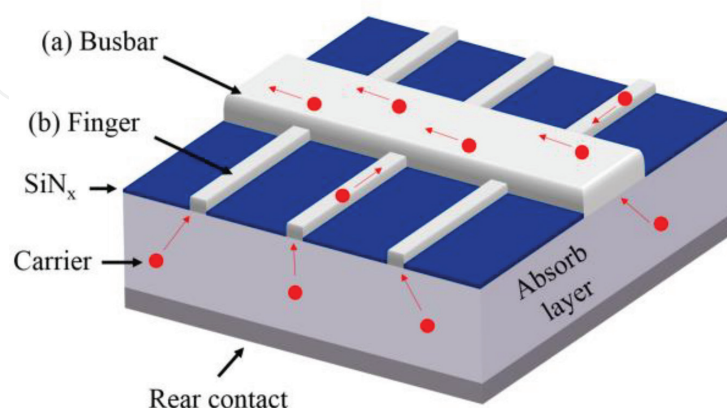
## 1. Introduction

In photovoltaic industries, screen printing is the most dominant metallization technique for silicon-based solar cell fabrication as it is quick and simple. As a material of front contact, silver is the favorable metal since it has high conductivity [1] and is chemically inactive. However, screen printing with silver paste is the most expensive portion in cell production

after the silicon material cost [2]. Therefore, reducing the amount of silver consumption per cell or replacing silver to other metal materials is a significant research area.

According to the international technology roadmap for photovoltaic (ITRPV) published in 2016, silver consumption per cell will decrease until 40 mg/cell in 2026 with developments of pastes and screens, which is around 40% lower than now (95 mg/cell) [3]. On the other hand, substituting silver for copper has been actively researched since the cost of copper is cheaper than silver (approximately a 50 times) and has a similar conductivity (silver:  $1.6 \mu\Omega\text{-cm}$ , copper:  $1.7 \mu\Omega\text{-cm}$ ) [4, 5]. In order to share new information and go over the technical limitations, workshops for the metallization of crystalline silicon solar cells have been organized since the first workshop in Utrecht, Netherlands, in 2008 [6].

Researches concerning copper contact mainly have been carried out by the plating technique due to its various advantages, such as high aspect ratio and low contact resistance, which result in a high-efficiency solar cell over 21% [7–12]. Meanwhile, the application of screen-printable copper paste on solar cells has been studied as it can be easily applied to the established cell production line. In the case of the copper paste, copper particles cannot be deposited directly on the emitter, because the copper atoms have fast diffusion velocity and acts as a deep-level impurity in the crystalline silicon solar cell [13–18]. The copper atoms in the silicon produce generation and recombination centers and degrade the minority carrier lifetime of the crystalline silicon solar cells [11, 19–21]. Accordingly, most of the copper pastes on the solar cells were printed above the passivation layer as a busbar, which is called “passivated busbars”, while the silver paste fingers contacted the silicon. **Figure 1** shows the fingers and a busbar of the solar cell that are printed by silver paste. Similar to the finger, the role of the busbar on the solar cell is a collection of charge carriers generated by incident light in the absorb layer. The busbar is also connected to the soldered ribbon to extract carriers out of the device. To connect a busbar with a ribbon, the busbar should be printed with similar width of the ribbon which is usually 1.5 mm on the commercial type of solar cells. Accordingly, researchers have tried to apply copper paste only for the busbar since most of the silver paste usage is for the busbar, while the fingers were still printed by silver paste or deposited by the plating technique.



**Figure 1.** Carrier collection by the screen-printed silver (a) busbar and (b) finger [26].

Nonetheless, it is possible that the copper paste can be in direct contact with the silicon if the copper particles are coated with barrier layers in order to prevent copper from diffusing into the silicon. Another issue of copper in the application to the paste form is that copper tends to oxidize easily during thermal treatment [13, 22–25]. Since copper oxide shows an electrically nonconductive characteristic, it will increase the series resistance in the solar cells. Due to these reasons, copper paste has been continuously researched by several institutes and companies in order to overcome such issues. Section 2 deals with research trends of the copper paste components and promising coating techniques of copper powder for better reliability. Afterwards, Section 3 discusses appropriate curing conditions of polymer-based copper paste and the results of copper paste application to the silicon solar cells.

## 2. Copper paste developments for the crystalline silicon solar cells

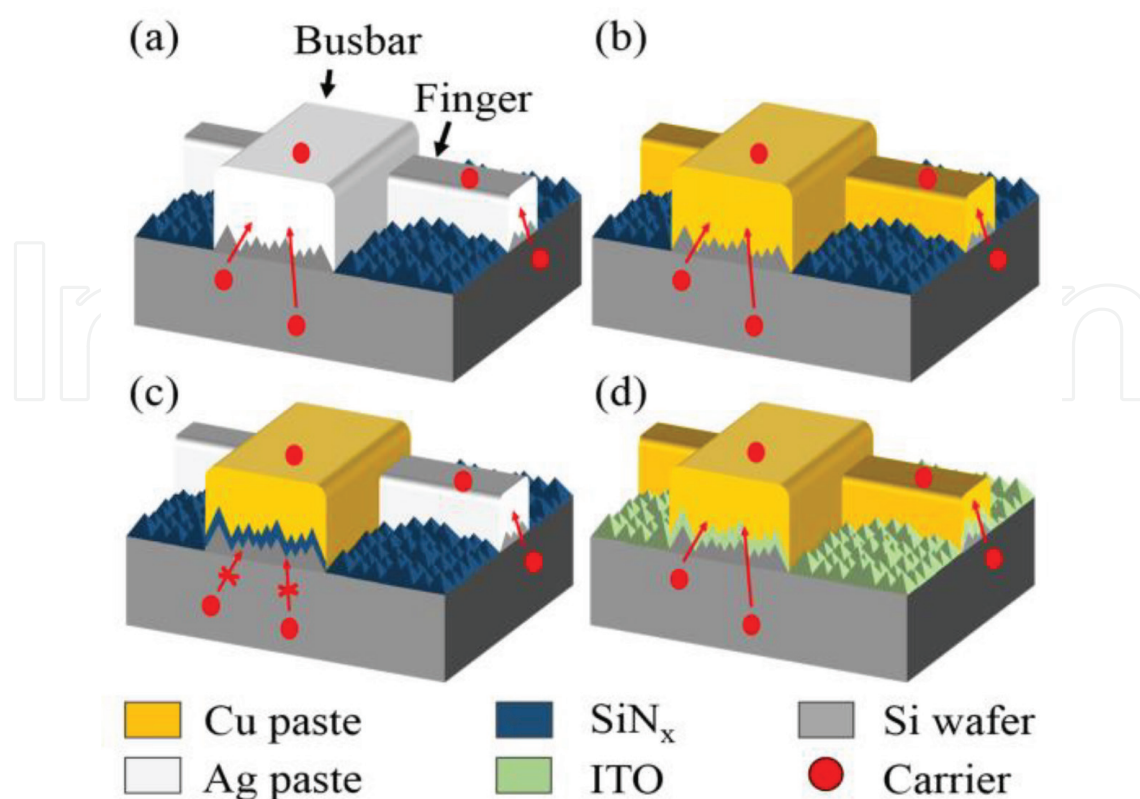
In the 1990s, copper paste was researched for the application of integrated circuits, such as print circuit boards, because copper has a high electrical conductivity, a high thermal conductivity, excellent solderability, and a low electron migration [27–29]. With the increase in circuit density, properties of copper paste needed to be improved. The researched topics were mainly focused on optimizing the size of metal particles to enhance the density and printability of paste [30, 31]. Recently, copper paste has been developed for the application of the crystalline silicon solar cells as the low-cost front contact.

### 2.1. Structure of metallized solar cells with screen-printed pastes

Copper paste is generally compared to silver paste since it is a dominant material for the front metallization of the crystalline silicon solar cell. In order to apply copper paste to the solar cells, the properties of copper paste, such as printability and solderability, need to have similar or better characteristics than silver paste. Electronic pastes are generally composed of conductor metal (Ag, Au, Pd, Cu, etc.), glass frits, and organic vehicle [32, 33]. One of the important components of the conventional silver paste for the front contact of the crystalline silicon solar cell is glass frits. In case of the crystalline silicon solar cells based on the silver paste, the dielectric layer, which is usually silicon nitride ( $\text{SiN}_x$ ), is fired-through above  $600^\circ\text{C}$  and the silver particles contact the emitter (**Figure 2(a)**).

On the other hand, if the copper paste has the same process as the silver paste, the diffused copper can adversely effect on the characteristics of the solar cell as we mentioned earlier. Thus, for applying copper paste to the crystalline silicon solar cell, copper particles in the paste need to be coated by barrier layers. In this case, the copper paste can be fired at a similar temperature range as the silver paste and contact the emitter (**Figure 2(b)**). Otherwise, the contact should be formed without penetrating the  $\text{SiN}_x$  layer (**Figure 2(c)**) by applying the curing type copper paste which does not need the glass-frits components for the fired-through contact.

Silicon heterojunction (SHJ) solar cells have typically a low process temperature limit ( $\sim 250^\circ\text{C}$ ) because high-temperature annealing processes can degrade the passivation of the



**Figure 2.** (a) Conventional silicon solar cell contact with silver paste, (b) contact with firing-type copper paste, (c) contact with curing-type copper paste, and (d) contact with curing-type copper paste on the SHJ solar cell [26].

hydrogenated amorphous silicon (a-Si:H) due to the hydrogen effusion during the annealing [34]. For this reason, the curing-type copper paste, where low temperature is generally required, is beneficial to the SHJ solar cells. Also, if copper paste is printed on the indium tin oxide (ITO) layer of the SHJ solar cell (**Figure 2(d)**), ITO can act as a diffusion barrier for preventing copper diffusion [35]. The next section discusses detail components of the copper pastes for the application of the solar cells by categorizing the annealing temperature of the paste.

## 2.2. Copper paste for high-temperature annealing (firing type)

In 2011, a copper paste that is chemically and metallurgically similar to conventional silver paste was developed by Applied Materials, Inc. [36]. The copper paste can be fired through a  $\text{SiN}_x$  layer and the metal particles directly contact silicon (**Figure 2(b)**). The main components and possible materials of the invented copper paste are listed in **Table 1**. The invented technique involves copper-containing particles being encapsulated by additional layers of metal and alloys to restrict oxidation and diffusion of copper during the firing. For improving the oxidation resistance of copper, alloying copper with other metals (Ti, Mg, Al, Pd, Ag, Ni, Cr, and Zr) has been researched [37–40]. The Cu-Ag alloy is estimated as the best materials for improving oxidation resistance with only a slight reduction in electrical conductivity [41]. The paste of this group also uses doped copper or copper alloys rather than pure copper particles,

Components	Materials	Purposes
Metal powder	Doped copper (aluminum, magnesium, etc.), copper alloys (CuSn, CuAg, CuNi, CuZn, etc.)	To have conductive property
Polymer resin	Ethylcellulose	To enable printing of copper-containing particles
Glass frits	Lead oxide (PbO <sub>x</sub> ), silicon oxide (SiO <sub>2</sub> ), alumina (Al <sub>2</sub> O <sub>3</sub> ), boron trioxide (B <sub>2</sub> O <sub>3</sub> ), zirconia (ZrO <sub>2</sub> ), zinc oxide (ZnO), bismuth oxide (Bi <sub>2</sub> O <sub>3</sub> ), strontium oxide (SrO), titanium oxide (TiO <sub>2</sub> ), and lanthanum oxide (La <sub>2</sub> O <sub>3</sub> )	To pass through a passivation layer and promotes adhesion to the substrate
Solvents	$\alpha$ -Terpineol, toluene, ethanol	To tune viscosity characteristics

**Table 1.** Components and possible materials of the copper paste for high-temperature annealing.

because alloying elements in copper reduce the contact with oxygen. Generally, the polymer resin acts as a binder to enable printing of the encapsulated copper-containing particles and is typically removed during the firing by oxidation.

**Figure 3** shows three levels of encapsulation for preventing copper particles from oxidation and diffusion. Simply, the copper-containing particle can be coated by oxidation barrier layers. Also, a metallization barrier layer can be used under the oxidation barrier since the oxidation layer can form an alloy with the inside material. Moreover, a diffusion barrier can directly surround the copper-containing particle for a more perfect encapsulation. The possible materials for the encapsulation layer are listed in **Table 2**.

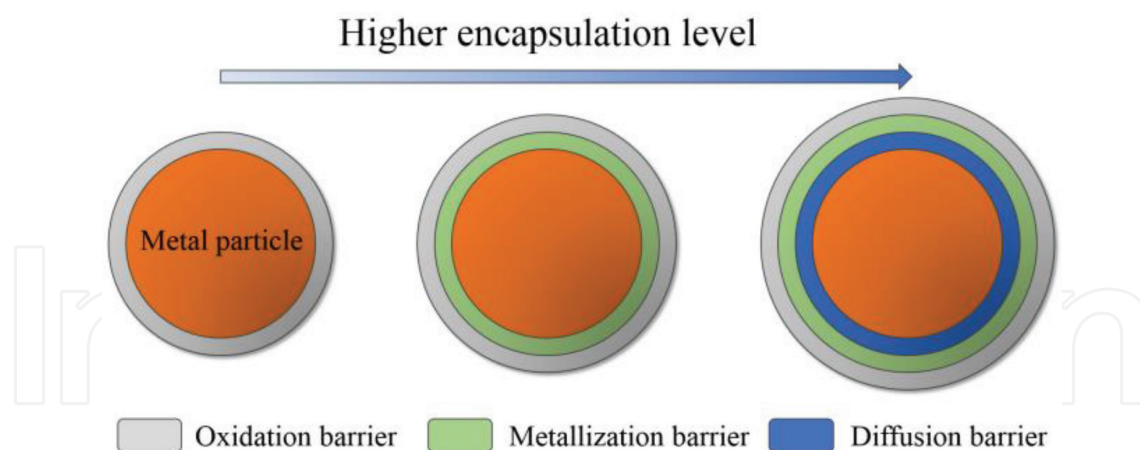
### 2.3. Copper paste for low-temperature annealing (curing type)

In order to create a solderable surface on the ITO of the SHJ solar cells, polymer-based silver pastes were commonly used in the solar cell industry, because silver has a low contact resistivity on ITO and low line resistances. However, reactions between polymer and solder flux during the annealing result in a “solder leaching” problem. If the screen-printed paste is dissolved in the solder material due to the solder leaching, it leads to low adhesion and high contact resistivity between paste and solder material.

Using copper instead of silver, as a metal powder in the polymer-based paste, is a good solution in order to overcome the issue of solderability, because copper produces a comparable solderability and resistance at a much lower price [42]. For these reasons, polymer-based copper paste for low-temperature annealing has been researched as a promising product in the future with the fact that the SHJ solar cells have become common in the PV industry [43–46]. From now on, the components and properties of the curing-type copper pastes from some groups will be discussed.

#### 2.3.1. Dow Corning

Dow Corning reported papers and patents about a curing-type copper paste and the applicable solar cell structures [47–51]. The curing is referred to as the hardening of polymer materials



**Figure 3.** Cross-sectional views of encapsulated copper-containing particles with single and multi-barrier layer.

Encapsulation layer	Oxidation barrier	Metallization barrier	Diffusion barrier
Possible materials	Silver (Ag), nickel (Ni), and zinc (Zn)	Nickel (Ni), titanium (Ti), titanium nitride (TiN), tungsten (W), titanium-tungsten (TiW), cobalt (Co), tungsten doped cobalt (Co:W), molybdenum (Mo), tantalum (Ta), and chromium (Cr)	

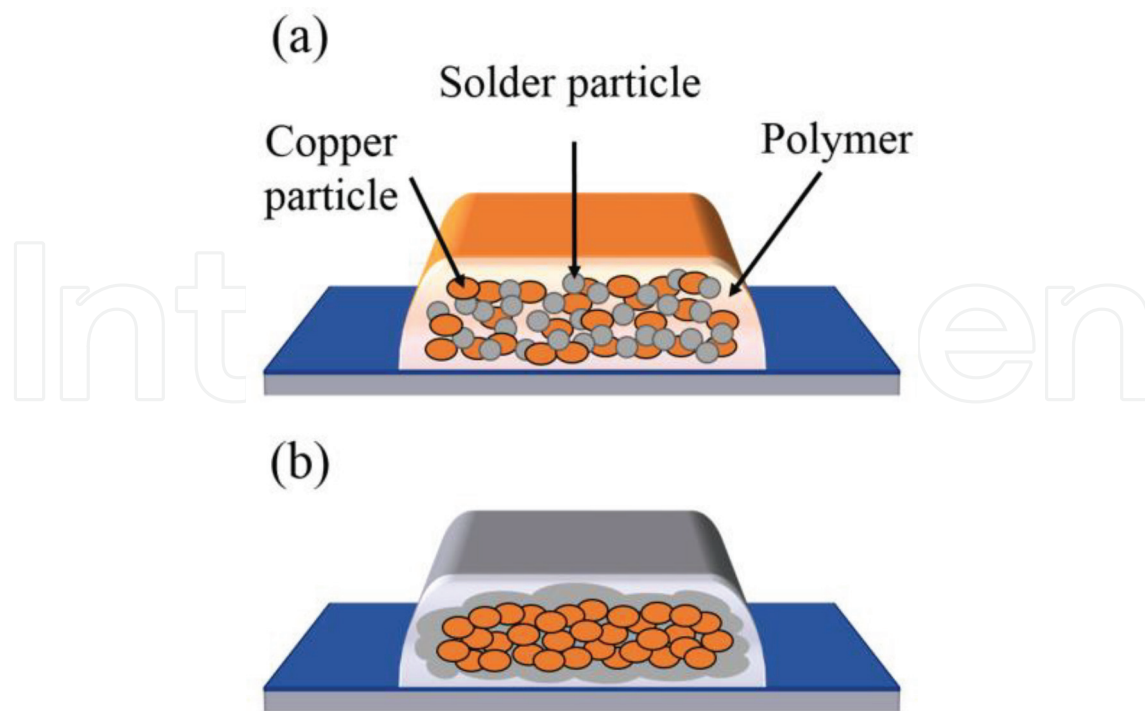
**Table 2.** The possible materials of each encapsulation layer for copper-containing particles.

by cross-linking polymer chains that can be processed by heating at a low temperature under 300°C. The copper paste consists of metal powder, solder powder (lower melting temperature than that of the metal powder), a polymer, a solvent, a cross-linking agent, and additives. The solder powder comprises at least one of a tin-bismuth (SnBi) alloy, a tin-silver (SnAg) alloy, or combinations of them. The polymer and the carboxylated polymer are made of an epoxy resin and an acrylic polymer, respectively. The cross-linking agent (or catalyst) can be chosen from carboxylated polymers, dimer fatty acids, and trimer fatty acids. Among the dimer fatty acid, dicarboxylic acid and monocarboxylic acid are useful for fluxing the metal powder and cross-linking the polymer. Moreover, a solvent and an adhesion promoter can be included as additive components.

This copper paste is used to form a busbar of the conventional crystalline silicon solar cell without a fired-through process. **Figure 4** shows that the printed busbar has a brown-red color due to the copper particles. Afterwards, the color of the busbar changes to gray after the curing process because the copper particles are coated by the solder. The cells with the copper busbar have a higher front surface minority carrier lifetime than the cells with the silver fired-through busbar since the covered area under the busbar is fully passivated. The detail characteristics will be mentioned in Section 3.

### 2.3.2. National Institute of Advanced Industrial and Scientific Technology (AIST)

A research group in the AIST also reported a similar concept of the copper paste as the Dow Corning's copper paste. Their copper paste, which is called "copper-alloy paste," is composed



**Figure 4.** Dow Corning's screen-printable copper paste: (a) after printing and (b) after curing [26].

of conductive metal particles, low melting point alloy (LMPA), thermosetting polymer, and solvent [52]. During the curing process, the molten LMPA particles form alloy with the copper particles and surround the copper particles to prevent oxidation. In particular, the LMPA allows the curing process to set the temperature below 200°C without any reductive conditions unlike the conventional silver paste. The result of the differential scanning calorimetry (DSC) shows that the melting point of the LMPA is 143°C. The peak of the DSC graph is very sharp since the LMPA had a nano-level uniformity. Moreover, the copper-alloy paste shows better self-leveling and resolution than the conventional silver paste after the screen-printing process on a textured silicon wafer.

Also, the copper paste from this group shows decent reliability after printing as a busbar on p-type crystalline silicon [53]. The samples were tested by the damp heat test (DHT) and thermal cycling test (TCT) before and after the encapsulation with the "sandwich" structure (glass/EVA/cell/EVA/backsheet) according to the IEC61215 standards. The results of both DHT and TCT show degradation less than 5% of the initial values in all parameters ( $V_{oc}$ ,  $J_{sc}$ , FF,  $P_{max}$ , etc.) before and after encapsulation. Although the surface of the copper electrode without encapsulation is oxidized after the DHT test, the copper oxide layer acts as a semi-passivation layer that postpones inner oxidation. Moreover, the copper particles in their paste do not diffuse into the silicon even after an hour of annealing at 400°C due to the polymer barrier layer.

### 2.3.3. Samsung Electro-Mechanics Co., Ltd.

The invented copper paste was focused on the nano-particle size copper powder, especially for substrates (such as a transparent conductive oxide (TCO), a polymer, a glass plate, and a printed circuit board), which have difficulties in applying high-temperature processes [54, 55].



The average particle size of copper is around 150 nm, and the surfaces of the copper particles are coated with a capping material which can be fatty acid or fatty amine. The nano-size copper powder is used either solely as a metal powder or with different sizes of copper particles, such as a flake powder and a spherical powder. The flake powder has a particle size of 1–20  $\mu\text{m}$  and the spherical powder has a 0.1–5- $\mu\text{m}$  particle size. When the nano-powder is mixed with other types of powder, it first dissolves during the annealing and then helps to connect between the larger copper particles. Because of this nano-size effect, this copper paste can enhance conductivity. The detailed candidates for binders and additives are also presented in the patent. Consequently, the copper particle at 150-nm size decreases the annealing temperature of the paste and makes it possible to form electrodes at a low temperature of 200°C.

#### 2.3.4. Institute of Nuclear Energy Research (INER)

Recently, the INER reported an antioxidant copper paste [56, 57]. The antioxidant copper nanoparticles are synthesized by a wet chemical reduction process which requires copper hydroxide ( $\text{Cu}(\text{OH})_2$ ), polyvinylpyrrolidone (PVP), and ascorbic acid. Afterwards, the antioxidant copper nanoparticles are transferred to the paste form and printed onto the ITO layer of SHJ solar cells, followed by low-temperature annealing (<300°C). Compared to commercial silver pastes as a reference, this copper paste shows a twofold increase in sheet resistance ( $\sim 30 \text{ m}\Omega/\text{sq}$ ) on the 16  $\mu\text{m}$  of printed films. However, the duration of copper paste annealing is 1/12 of that of silver paste. Also, reserving samples for 180 days without strict oxygen protection shows no peaks of oxide impurities after XRD characterization, which means that the copper film is relatively stable against oxidation at least at an X-ray detection level.

### 2.4. Promising techniques for high performance of copper paste

#### 2.4.1. Coating of copper powder with nano-silica

In order to apply copper on conductive paste, it requires high-purity crystalline non-agglomerated copper powder, which is free from surface oxidation [58, 59]. Using silica as a coating material of copper powder can enhance colloidal properties and functions by using rational core-shell shapes [60]. Dong et al. coated nano-copper powder with nano-silica by using a sol-gel process to improve the dispersion of the glass in the paste, the density of films, and the bonding behavior between the film and the substrate [61]. The printed films by using the copper paste after sintering at 910°C show no significant change in the density of the surface morphology and sheet resistance with the contents of silica from 0.5 to 2 wt%. However, the bonding between the film and the substrate improves with 2 wt% of silica contents in copper powder. The reason is that the proper amount of silica contents can induce the capillary effects and surface sorption effects which is beneficial to bond the film closely on the substrate. The properties of silica-coated copper powder will be able to improve the bonding of the high-temperature annealing copper paste on the silicon wafers.

#### 2.4.2. Coating of copper powder with cobalt-catalyzed carbon nanofibers

Even though the properties of polymer-based copper paste have been improved by many research, it is still difficult to achieve high conductivity and reliability as silver paste due to

the relatively low conductivity of the polymers [62–66]. In addition, using nanoscale copper particles for decreasing curing temperature also have issues of powder production step, such as controlling the size of particles [67], low oxidation resistance of particles [68, 69], and cost-effectiveness [70]. For this reason, the development of copper particles, which are coated by a carbon-based material, has been interested by many researchers, because carbon shells can act as the shields to protect the copper particles from oxidation [71–79]. In addition, there have been studies for the development of copper paste or ink, which do not require inert atmosphere and lower temperature, but they still have challenges to overcome [80–83].

In order to improve oxidation resistance of copper particles and make curing process possible in air, Ohnishi et al. coated copper-cobalt alloy particles with cobalt-catalyzed carbon nanofibers (CNFs) which is called “hybrid copper particles (HCuP)” [84]. The paste, which is made by the sea urchin-shaped copper particles, shows great reliability of resistivity even after a DHT test. The good electrical properties of this copper paste might come from an anti-oxidation effect of CNFs. Moreover, the cobalt nano-precipitates on the surface of the particles can be regarded as a conductive path. This approach possibly can improve the reliability of copper pastes by curing without strictly controlled inert atmosphere.

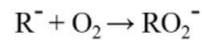
### 3. Application of copper paste on crystalline silicon solar cells

#### 3.1. Curing conditions of copper paste for high electrical properties

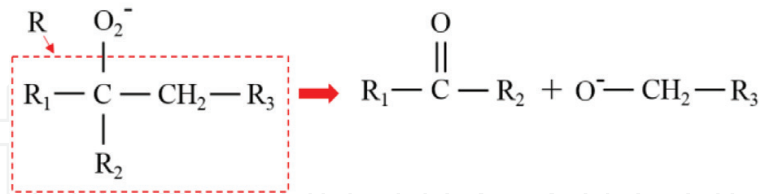
Low-temperature annealing paste generally contains polymer as a component. Accordingly, the properties of these pastes highly depend on the polymerization quality during the curing process. The curing process is carried out at a lower-temperature range than the firing process, which is generally used for the conventional silver paste. *Rehm thermal systems GmbH* and *Fraunhofer Institute for Ceramic Technologies and Systems* reported the effect of curing conditions on properties of the electrode which is printed with the polymer-based copper paste [22, 42, 62, 85]. By using an inert inline drying system, they show that curing with a high nitrogen atmosphere and temperature at 200°C can significantly decrease the resistance of copper paste electrode [42].

The main reason of the resistance reduction is that the cross-linking reactions of polymer chains are sensitive to the oxygen concentration, because the oxygen disturbs the linking process between the polymer chains. **Figure 5** shows the reactions of degradation of the polymer chain which frequently occurs in a high oxygen atmosphere. Oxygen easily reacts with most organic radicals which form “peroxidic radicals” [86]. The peroxidic radicals can suffer the polymerization reactions or the chain processes. As one of the most frequent reactions, an oxidative degradation breaks the polymer chains by initiating the decomposition of the peroxidic radicals. If the polymerization process is carried out in this circumstance, oxygen presence will decrease the cross-linking yield of polymers in the pastes. Therefore, the inert curing atmosphere with low concentration of the oxygen is significant in order to make an intensified polymerization and increase the compression of the metal particles. The restrained oxidation of the metal particles can also be a possible reason.

*Reaction 1: peroxidic radicals formation*



*Reaction 2: decomposition of polymer chain*



**Figure 5.** Reactions of polymer chain decomposition by oxygen.

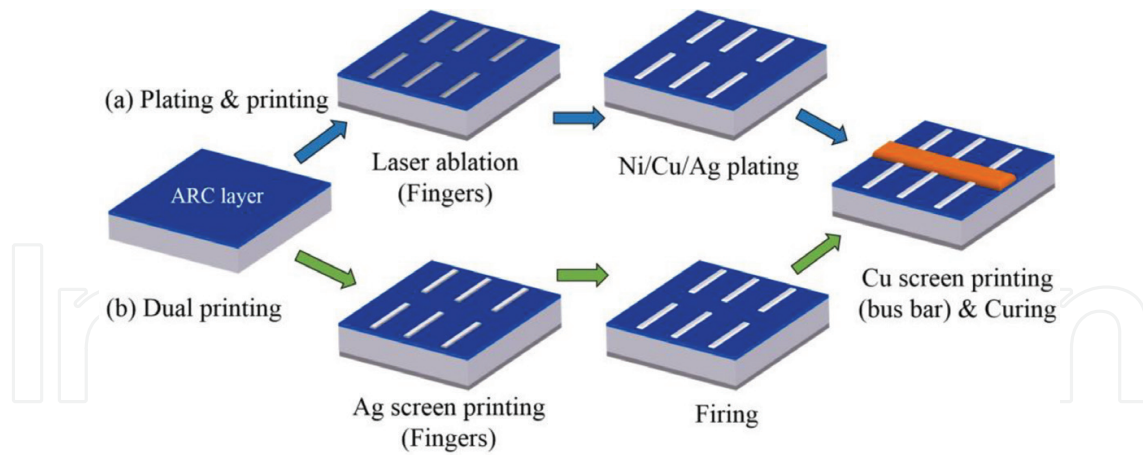
In case of the heat transfer method, a radiation method is more beneficial for the lower resistance of electrode than a convection method [62]. Moreover, the minimum resistance and decent adhesion can be obtained by increasing the processing time [22]. Consequently, this group confirmed that the polymer-based copper paste, which was annealed by the inert curing, can improve conductivity and mechanical stability of the polymer-based copper paste by achieving 19.96% efficiency with the SHJ solar cell, even though the fill factor (FF) is still lower than that of silver paste-printed cells.

### 3.2. Potential of copper paste on the silicon solar cells as passivated busbars

Some research groups have tried to apply their own copper paste to solar cells. The copper pastes were printed as passivated busbars that required forming busbars and fingers separately. As **Figure 4** shows, fingers only electrically contact silicon by using either fired-through silver paste (**Figure 6(b)**) or the plating of Ni/Cu/Ag metal stack after the laser ablation opening of  $SiN_x$  layer (**Figure 6(a)**). Afterwards, the busbar is printed on the  $SiN_x$  layer and partially contacts the fingers followed by a curing process under  $250^\circ C$ . Since the busbars do not directly contact the silicon, recombination region under the busbars is removed. Light I-V performances of the solar cells with copper paste busbar are summarized in **Table 3**. On the reference cells, either the screen-printed silver paste contact or the Ni/Cu/Ag-plated contact was wholly used for the busbars and fingers. Generally, the reduced recombination on the front side contributes to an increase open circuit voltage ( $V_{oc}$ ) compared to the cells without passivated busbar.

Dow Corning and IMEC evaluated characteristics of various cell structures by applying their own low-temperature ( $\sim 250^\circ C$ ) copper paste for the passivated busbars. The research results show a slight increase of  $V_{oc}$  (0.3 mV) with an industrial level passivated emitter solar cell (PESC) by reducing the recombination region under the busbars. Compared to the conventional silver paste solar cell, the passivated copper busbar solar cell has a lower average fill factor (FF) due to the higher lateral resistivity of the copper busbar. However, the busbar resistivity does not have an effect on the FF in the module level performance since most of lateral current flows through the conductive soldered tab.

This group also evaluated combinations of printable conductive copper paste with higher efficiency solar cell structures, such as passivated emitter and rear cell (PERC) and passivated



**Figure 6.** Front metallization process flows for the passivated copper busbar: (a) plating and printing, and (b) dual printing [26].

Institute	Year	Cell type	Ref. contact	$\eta$ [%] (gain)	$V_{oc}$ [mV] (gain)	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%] (gain)	Annealing temp.	Ref.
Dow Corning	2014	p-PESC (SE)	SP*-Ag	18.8 (-0.07)	640.4 (+0.3)	37.2	78.9 (-0.5)	~250°C	[47]
Dow Corning	2015	p-PERC	Plated-Ni/ Cu/Ag	20.4 (+0.1)	667.5 (+6.1)	38.7	79.0 (+0.3)	~250°C	[48]
Dow Corning	2015	n-PERT	Plated-Ni/ Cu/Ag	20.7 (0)	663.3 (+4.9)	39.2	79.5 (0)	~250°C	[48]
Meiji Univ.	2015	n-PERT (bifacial)	SP-Ag	20.5 (+0.7)	659.0 (+3.0)	40.8	76.3 (+2.0)	—	[87]
Tokyo Univ.	2012	p-PESC (mc-Si)	SP-Ag	16.2 (+0.1)	617.0 (-2.0)	34.3	76.3 (+0.1)	<200°C	[88]

\*SP: screen printed.

**Table 3.** Performance of various solar cell structures with the passivated copper busbar and gains compared to their reference contact.

emitter and rear totally diffused (PERT). By applying a copper paste busbar with the plating and printing process as depicted in **Figure 6(a)**, both structures improved 6.1 mV, 4.9 mV of  $V_{oc}$ , respectively, and the PERC structure especially had a 0.1% higher median conversion efficiency than the reference group. Also, the FF of the passivated busbar cells had increased since the laser ablation and the nickel silicide decreased the shunt resistance of entirely plated cells. In the case of the current density, the passivated busbar cell had a slightly lower value even though the series resistance of both the printed busbar and the plated busbar almost had no difference since the plated busbar had a higher aspect ratio (fine line width).

Nakamura et al. at the Meiji University applied copper paste on the n-type bifacial PERT cell and successfully obtained over 20% efficiency by preceding  $V_{oc}$  and FF of the silver-printed cell. Also, Yoshiba et al. at the Tokyo University compared the I-V performances on the

multi-crystalline silicon solar cell by printing a low melting point alloy (LMPA) copper paste. Although  $V_{oc}$  was decreased, copper-printed cell had a 0.1% absolute efficiency gain due to the higher FF. In most of the experiments for confirming applicability of copper paste on solar cell fabrication, the results show the possibility of reduction of metallization cost and cell performance improvement by replacing the standard silver-printed electrode.

#### 4. Summary and outlook

In this chapter, a detailed overview of the copper paste developments for the solar cell application has been presented. The main issues of developing copper paste are prohibition of the oxidation of copper during annealing and the diffusion into the silicon substrate. In case of the glass-frit-based copper paste (firing type), the copper particles are coated with metal or alloy layers to prevent the diffusion and the oxidation. However, the firing-type copper paste still has a higher possibility of diffusion than the polymer-based copper paste (curing type) since the copper particle comes in direct contact with the silicon. In case of the curing-type copper paste, the diffusion of copper particles is well blocked since the surrounding polymer acted as a barrier layer. Also, the oxidation of copper can be prevented by the polymer shield or using antioxidant copper particles. Moreover, DHT and TCT of the copper paste confirm the reliability on the solar cells with a small amount of degradation (<5%).

For further improvement of the copper paste properties, recently reported coating materials and techniques for the copper powder have been introduced. In case of the nano-silica coating on copper powder, the bonding strength of paste on the substrate was improved by promoting capillary effects and surface sorption effects. Also, the air-curable hybrid copper particles, which were coated by cobalt-catalyzed-CNFs, lead to a great resistance reliability of the printed copper paste.

With respect to the curing conditions, the experimental results revealed that the inert atmosphere helps to form a denser copper electrode by restricting the contact between the polymers and the oxygen. Thereby, the compressed copper particles due to the intensified polymerization decrease the resistivity of the printed copper film. However, the inert curing condition requires a great deal of nitrogen gas for purging oxygen in the furnace. At the industrial level, the nitrogen consumption can adversely affect the manufacturing cost of the solar cells. Therefore, the optimum curing process for less consumption of nitrogen gas and inexpensive coating technique of copper particles need to be further developed.

To date, polymer-based copper paste showed a high potential with 20.7% conversion efficiency by applying it to the n-PERT structure solar cells. As well as the result of the PERT structure, the copper paste application to SHJ solar cells has a higher potential because the ITO layer acts as a diffusion barrier to prevent copper at a low curing temperature. Also, the use of copper paste, as the passivated busbars, requires an additional printing, and the annealing step after the silver fingers and aluminum rear contact are formed. Accordingly, the SHJ solar cells are more profitable for the application of copper paste from an economic point of view.

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## References

- [1] Park K, Seo D, Lee J. Conductivity of silver paste prepared from nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2008;**313**:351-354
- [2] Powell DM, Fu R, Horowitz K, Basore PA, Woodhouse M, Buonassisi T. The capital intensity of photovoltaics manufacturing: Barrier to scale and opportunity for innovation. *Energy & Environmental Science*. 2015;**8**:3395-3408
- [3] International Technology Roadmap for Photovoltaic (ITRPV). Available from: <http://www.itrpv.net> [Accessed: 2016-Mar]
- [4] London Bullion Market Association (LBMA). Available from: <http://www.lbma.org.uk/home> [Accessed: 2017-Mar]
- [5] London Metal Exchange. Available from: <https://www.lme.com/metals/non-ferrous/nickel> [Accessed: 2017-Mar]
- [6] Workshop on Metallization for Crystalline Silicon Solar Cells. Available from: <http://www.metallizationworkshop.info>
- [7] Horzel J, Bay N, Passig M, Sieber M, Burschik J, Kühnlein H, Brand A, Letize A, Lee B, Weber D, Böhme R. Low cost metallization based on Ni/Cu plating enabling high efficiency industrial solar cell. In: *Proceeding of the 29th European Photovoltaic Solar Energy Conference and Exhibition; 2014; Amsterdam, Netherland*. pp. 507-512
- [8] Bay N, Horzel J, Passig M, Sieber M, Burschik J, Kühnlein H, Bartsch J, Brand A, Mondon A, Eberlein D, Völker C, Gutscher S, Letize A, Lee B, Weber D, Böhme R. Reliable contact formation for industrial solar cell by laser ablation and Ni/Cu plating. In: *Proceedings*

of the 29th European Photovoltaic Solar Energy Conference and Exhibition; 2014; Amsterdam, Netherland. pp. 1272-1276

- [9] Hernández JL, Adachi D, Yoshikawa K, Schroos D, Assche EV, Feltrin A, Valckx N, Menou N, Poortmans J, Yoshimi M, Uto T, Uzu H, Hino M, Kawasaki H, Kanematsu M, Nakano K, Mishima R, Kuchiyama T, Koizumi G, Allebé C, Terashita T, Hiraishi M, Nakanishi N, Yamamoto K. High efficiency copper electroplated heterojunction solar cells. In: Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition; 2012; Frankfurt, Germany. pp. 655-656
- [10] Papet P, Hermans J, Söderström T, Cucinelli M, Andreetta L, Bätzner D, Frammelsberger W, Lachenal D, Meixenberger J, Legradic B, Strahm B, Wahli G, Brok W, Geissbühler J, Tomasi A, Ballif C, Vetter E, Leu S. Heterojunction solar cell with electroplated Ni/Cu front electrode. In: Proceedings of the 28th European Photovoltaic Solar Energy Conference; 2013; Paris, France. pp. 1976-1979
- [11] Bartsch J, Mondon A, Kamp M, Kraft A, Wendling M, Mehling M, Wehkamp N, Jawaid M, Lorenz A, Clement F. Copper as conducting layer in the front side metallization of crystalline silicon solar cells—Challenges, processes and characterization. Proceedings of the 2nd Workshop on Metallization for Crystalline Silicon Solar Cells—Status, Trends and New Directions, Constance, Germany, Konstanz, Germany; 2010. pp. 32-37
- [12] Metz A, Adler D, Bagus S, Blanke H, Bothar M, Brouwer E, Dauwe S, Dressler K, Droessler R, Droste T. Industrial high performance crystalline silicon solar cells and modules based on rear surface passivation technology. *Solar Energy Materials and Solar Cells*. 2014;**120**:417-425
- [13] Istratov AA, Weber ER. Physics of copper in silicon. *Journal of The Electrochemical Society*. 2002;**149**:G21-G30
- [14] Brotherton S, Ayres J, Gill A, Van Kesteren H, Greidanus F. Deep levels of copper in silicon. *Journal of Applied Physics*. 1987;**62**:1826-1832
- [15] Kaimao C, Zhongan W. Deep levels related to copper in silicon. *Journal of Electronics (China)*. 1988;**5**:285-293
- [16] Aboelfotoh M, Svensson B. Copper passivation of boron in silicon and boron reactivation kinetics. *Physical Review B*. 1991;**44**:12742
- [17] Murarka SP, Hymes SW. Copper metallization for ULSL and beyond. *Critical Reviews in Solid State and Materials Sciences*. 1995;**20**:87-124
- [18] Murarka SP. Advanced materials for future interconnections of the future need and strategy: Invited lecture. *Microelectronic Engineering*. 1997;**37**:29-37
- [19] Schibli E, Milnes A. Deep impurities in silicon. *Materials Science and Engineering*. 1967;**2**:173-180
- [20] Weber ER. Transition metals in silicon. *Applied Physics A: Materials Science & Processing*. 1983;**30**:1-22

- [21] Ur Rehman A, Lee SH. Crystalline silicon solar cells with nickel/copper contacts. In: *Solar Cells—New Approaches and Reviews*. InTech; 2015
- [22] Clement C, Bell H, Vogg F, Rebenklau L, Gierth P, Partsch U. Inert drying system for copper paste application in PV. *Energy Procedia*. 2013;**38**:423-429
- [23] Mimura K, Lim J-W, Isshiki M, Zhu Y, Jiang Q. Brief review of oxidation kinetics of copper at 350 C to 1050 C. *Metallurgical and Materials Transactions A*. 2006;**37**:1231-1237
- [24] Xu X, Luo X, Zhuang H, Li W, Zhang B. Electroless silver coating on fine copper powder and its effects on oxidation resistance. *Materials Letters*. 2003;**57**:3987-3991
- [25] Jeong S, Woo K, Kim D, Lim S, Kim JS, Shin H, Xia Y, Moon J. Controlling the thickness of the surface oxide layer on Cu nanoparticles for the fabrication of conductive structures by ink-jet printing. *Advanced Functional Materials*. 2008;**18**:679-686
- [26] Lee SH, Lee DW, Lee SH. Review of conductive copper paste for c-Si solar cells. *Korean Journal of Metals and Materials*. 2017;**55**:637-644
- [27] Wu S. Preparation of ultra-fine copper powder and its lead-free conductive thick film. *Materials Letters*. 2007;**61**:3526-3530
- [28] Huang C-Y, Sheen SR. Synthesis of nanocrystalline and monodispersed copper particles of uniform spherical shape. *Materials Letters*. 1997;**30**:357-361
- [29] Sinha A, Das SK, Kumar TV, Rao V, Ramachandrarao P. Synthesis of nanosized copper powder by an aqueous route. *Journal of Materials Synthesis and Processing*. 1999;**7**:373-377
- [30] Ogawa T, Asai T, Itoh O, Hasegawa M, Ikegami A, Atoh K, Kobayashi T. New thick-film copper paste for ultra-fine-line circuits. *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*. 1989;**12**:397-401
- [31] Taylor BE, Tsuchiya M, Okabe C. Thick Film Copper Paste Composition. Google Patents; 1992
- [32] Brown O, Sridharan S. Lead-free and Cadmium-free Conductive Copper Thick Film Pastes. Google Patents; 2004
- [33] Brown O, Sridharan S. Lead-free and Cadmium-free Conductive Copper Thick Film Pastes. Google Patents; 2006
- [34] De Wolf S, Kondo M. Boron-doped a-Si: H/ c-Si interface passivation: Degradation mechanism. *Applied Physics Letters*. 2007;**91**:112109
- [35] Liu C, Liu W, Chen W, Hsieh S, Tsai T, Yang L. ITO as a diffusion barrier between Si and Cu. *Journal of the Electrochemical Society*. 2005;**152**:G234-G239
- [36] Gee JM. Cu Paste Metallization for Silicon Solar Cells. Google Patents; 2011
- [37] Li J, Li Y, Wang Z, Bian H, Hou Y, Wang F, Xu G, Liu B, Liu Y. Ultrahigh oxidation resistance and high electrical conductivity in copper-silver powder. *Scientific Reports*. 2016;**6**:39650



- [38] Li J, Mayer J, Colgan E. Oxidation and protection in copper and copper alloy thin films. *Journal of Applied Physics*. 1991;**70**:2820-2827
- [39] Kawamura G, Alvarez S, Stewart IE, Catenacci M, Chen Z, Ha Y-C. Production of oxidation-resistant Cu-based nanoparticles by wire explosion. *Scientific Reports*. 2015;**5**:18333
- [40] An BW, Gwak E-J, Kim K, Kim Y-C, Jang J, Kim J-Y, Park J-U. Stretchable, transparent electrodes as wearable heaters using nanotrough networks of metallic glasses with superior mechanical properties and thermal stability. *Nano Letters*. 2015;**16**:471-478
- [41] Kim KO, Kim S. Surface morphology control of Cu-Ag alloy thin film on W diffusion barrier by seedless electrodeposition. *Journal of Nanoscience and Nanotechnology*. 2016;**16**:11701-11706
- [42] Rebenklau L, Gieth P, Partsch U, Mehlich H, Hausmann J, Grimm M, Stein W, Bell H, Clement C, Vogg F. Low temperature interconnection techniques for high efficiency heterojunction solar cells. In: *Proceeding of the 27th European Photovoltaic Solar Energy Conference*; 2012
- [43] Heng JB, Fu J, Kong B, Chae Y, Wang W, Xie Z, Reddy A, Lam K, Beitel C, Liao C. > 23% high-efficiency tunnel oxide junction bifacial solar cell with electroplated Cu gridlines. *IEEE Journal of Photovoltaics*. 2015;**5**:82-86
- [44] Kleider J-P, Alvarez J, Brézard-Oudot A, Gueunier-Farret M-E, Maslova O. Revisiting the theory and usage of junction capacitance: Application to high efficiency amorphous/crystalline silicon heterojunction solar cells. *Solar Energy Materials and Solar Cells*. 2015;**135**:8-16
- [45] Mishima T, Taguchi M, Sakata H, Maruyama E. Development status of high-efficiency HIT solar cells. *Solar Energy Materials and Solar Cells*. 2011;**95**:18-21
- [46] Wang Q, Page M, Iwaniczko E, Xu Y, Roybal L, Bauer R, To B, Yuan H-C, Duda A, Hasoon F. Efficient heterojunction solar cells on p-type crystal silicon wafers. *Applied Physics Letters*. 2010;**96**:013507
- [47] Wood D, Kuzma-Filipek I, Russell R, Duerinckx F, Powell N, Zambova A, Chislea B, Chevalier P, Boulord C, Beucher A. Passivated busbars from screen-printed low-temperature copper paste. *Energy Procedia*. 2014;**55**:724-732
- [48] Wood D, Kuzma-Filipek I, Russell R, Duerinckx F, Powell N, Zambova A, Chislea B, Chevalier P, Boulord C, Beucher A. Non-contacting busbars for advanced cell structures using low temperature copper paste. *Energy Procedia*. 2015;**67**:101-107
- [49] Boulord C, Chevalier PM, Powell NE, Zambova AP. Composition and conductor formed therefrom. *Google Patents*; 2012
- [50] Albaugh JD, Beaucarne GDS, Powell NE, Zambova AP. Photovoltaic cell and method of forming the same. *Google Patents*; 2012
- [51] Beaucarne GDS, Powell NE, Tous L, Wood DA, Zambova AP. Photovoltaic cell and method of forming the same. *Google Patents*; 2012

- [52] Yoshida M, Tokuhisa H, Itoh U, Kamata T, Sumita I, Sekine S. Novel low-temperature-sintering type cu-alloy pastes for silicon solar cells. *Energy Procedia*. 2012;**21**:66-74
- [53] Tokuhisa H, Ise S, Morita S, Tsukamoto S, Tomita M, Yoshida M. Reliability of a printed cu busbar electrode on a conventional silicon solar cell. *Japanese Journal of Applied Physics*. 2015;**54**:08KD22
- [54] Kim DH, Oh SI, Kang SK, Jun BH, Song YA, Kim SJ, Chun BJ. Copper nano paste, method for forming the copper nano paste, and method for forming electrode using the copper nano paste. Google Patents; 2011
- [55] Lee YI, Kim DH, Kim JY, Kwon JH, Kim SE. Conductive paste composition for low temperature firing. Google Patents; 2013
- [56] Chang W-C, Weng L-W, Chuang C-K, Liang J-X, Yang T-N, Ma W-Y. The preparation of antioxidant copper paste and its application to silicon solar cells. *Journal of Nanoscience and Nanotechnology*. 2016;**16**:9125-9131
- [57] Ma W-Y, Chang W-C, Weng L-W, Liang J-X, Chung C-H, Yang T-N. The preparation of antioxidative copper pastes applicable to HIT solar cells metallization. In: 2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC); 2016; pp. 2949-2951
- [58] Sinha A, Sharma B. Preparation of copper powder by glycerol process. *Materials Research Bulletin*. 2002;**37**:407-416
- [59] Chow G, Kurihara L, Kemner K, Schoen P, Elam W, Ervin A, Keller S, Zhang Y, Budnick J, Ambrose T. Structural, morphological, and magnetic study of nanocrystalline cobalt-copper powders synthesized by the polyol process. *Journal of Materials Research*. 1995;**10**:1546-1554
- [60] Kobayashi Y, Inose H, Nakagawa T, Gonda K, Takeda M, Ohuchi N, Kasuya A. Control of shell thickness in silica-coating of au nanoparticles and their X-ray imaging properties. *Journal of Colloid and Interface Science*. 2011;**358**:329-333
- [61] Dong Q, Huang C, Duan G, Zhang F, Yang D. Facile synthesis and electrical performance of silica-coated copper powder for copper electronic pastes on low temperature co-fired ceramic. *Materials Letters*. 2017;**186**:263-266
- [62] Schörner S, Clement C, Bell H, Gierth P, Rebenklau L. Industrial inert drying system for high efficiency heterojunction solar cells. In: 31st European Photovoltaic Solar Energy Conference and Exhibition; 2015; Germany, Hamburg. pp. 887-889
- [63] Roncali J. Conjugated poly (thiophenes): Synthesis, functionalization, and applications. *Chemical Reviews*. 1992;**92**:711-738
- [64] Roncali J, Garnier F, Lemaire M, Garreau R. Poly mono-, bi-and trithiophene: Effect of oligomer chain length on the polymer properties. *Synthetic Metals*. 1986;**15**:323-331
- [65] Winter I, Reese C, Hormes J, Heywang G, Jonas F. The thermal ageing of poly (3, 4-ethylenedioxythiophene). An investigation by X-ray absorption and X-ray photoelectron spectroscopy. *Chemical Physics*. 1995;**194**:207-213

- [66] Yabuki A, Arriffin N. Electrical conductivity of copper nanoparticle thin films annealed at low temperature. *Thin Solid Films*. 2010;**518**:7033-7037
- [67] Khanna P, Gaikwad S, Adhyapak P, Singh N, Marimuthu R. Synthesis and characterization of copper nanoparticles. *Materials Letters*. 2007;**61**:4711-4714
- [68] Liu X, Zhou Y. Electrochemical synthesis and room temperature oxidation behavior of cu nanowires. *Journal of Materials Research*. 2005;**20**:2371-2378
- [69] Chen C-H, Yamaguchi T, Sugawara K-i, Koga K. Role of stress in the self-limiting oxidation of copper nanoparticles. *The Journal of Physical Chemistry B*. 2005;**109**:20669-20672
- [70] Foresti E, Fracasso G, Lanzi M, Lesci IG, Paganin L, Zuccheri T, Roveri N. New thiophene monolayer-protected copper nanoparticles: Synthesis and chemical-physical characterization. *Journal of Nanomaterials*. 2008;**2008**:62
- [71] Magdassi S, Grouchko M, Kamyshny A. Copper nanoparticles for printed electronics: Routes towards achieving oxidation stability. *Materials*. 2010;**3**:4626-4638
- [72] Pyo Y, Choi D, Son Y-H, Kang S, Yoon EH, Jung S-B, Kim Y, Lee CS. Fabrication of high quality carbonaceous coating on cu nanoparticle using poly (vinyl pyrrolidone) and its application for oxidation prevention. *Japanese Journal of Applied Physics*. 2016;**55**:055001
- [73] Bokhonov B, Novopashin S. In situ investigation of morphological and phase changes during thermal annealing and oxidation of carbon-encapsulated copper nanoparticles. *Journal of Nanoparticle Research*. 2010;**12**:2771-2777
- [74] Hao C, Xiao F, Cui Z. Preparation and structure of carbon encapsulated copper nanoparticles. *Journal of Nanoparticle Research*. 2008;**10**:47-51
- [75] Jacob DS, Genish I, Klein L, Gedanken A. Carbon-coated core shell structured copper and nickel nanoparticles synthesized in an ionic liquid. *The Journal of Physical Chemistry B*. 2006;**110**:17711-17714
- [76] Li H, Kang W, Xi B, Yan Y, Bi H, Zhu Y, Qian Y. Thermal synthesis of cu@ carbon spherical core-shell structures from carbonaceous matrices containing embedded copper particles. *Carbon*. 2010;**48**:464-469
- [77] Li J, C-y L. Carbon-coated copper nanoparticles: Synthesis, characterization and optical properties. *New Journal of Chemistry*. 2009;**33**:1474-1477
- [78] Gao MR, Xu WH, Luo LB, Zhan YJ, Yu SH. Coaxial metal nano-/microcables with isolating sheath: Synthetic methodology and their application as interconnects. *Advanced Materials*. 2010;**22**:1977-1981
- [79] Wang S, He Y, Liu X, Huang H, Zou J, Song M, Huang B, Liu C. Novel C/cu sheath/core nanostructures synthesized via low-temperature MOCVD. *Nanotechnology*. 2011;**22**:405704

- [80] Wang S, Huang X, He Y, Huang H, Wu Y, Hou L, Liu X, Yang T, Zou J, Huang B. Synthesis, growth mechanism and thermal stability of copper nanoparticles encapsulated by multi-layer graphene. *Carbon*. 2012;**50**:2119-2125
- [81] Lee YI, Lee KJ, Goo YS, Kim NW, Byun Y, Kim JD, Yoo B, Choa YH. Effect of complex agent on characteristics of copper conductive pattern formed by ink-jet printing. *Japanese Journal of Applied Physics*. 2010;**49**:086501
- [82] Eiroma K, Auvinen A, Forsman J, Hult E-L, Jokiniemi J, Koskela P, Sarlin J, Sipiläinen-Malm T, Tapper U. Development of conductive carbon coated copper nanoparticle inkjet fluid. *NIP & Digital Fabrication Conference*; 2011; pp. 458-461
- [83] Dang ZM, Zhang B, Li J, Zha JW, Hu GH. Copper particles/epoxy resin thermosetting conductive adhesive using polyamide resin as curing agent. *Journal of Applied Polymer Science*. 2012;**126**:815-821
- [84] Ohnishi S, Nakasuga A, Nakagawa K. Synthesis of copper particles covered with cobalt-catalyzed carbon nanofibers and their application to air-curable conductive paste. *Japanese Journal of Applied Physics*. 2017;**56**:07KD03
- [85] Gierth P, Rebenklau L, Paproth A, Bell H, Clement C, Vogg F, Sontag D, Mehlich H, Hausmann J, Stein W. Influence of inert curing on polymer paste characteristics on high efficiency heterojunction solar cells. In: *Proceedings of the 28th European Photovoltaic Solar Energy Conference and Exhibition*; Paris. pp. 460-463
- [86] Chapiro A. Radiation chemistry of polymers. *Radiation Research Supplement*. 1964;**4**:179-191
- [87] Nakamura K, Takahashi T, Ohshita Y. Novel silver and copper pastes for n-type bi-facial PERT cell. In: *31st European Photovoltaic Solar Energy Conference and Exhibition*; 2015; Hamburg, Germany. pp. 536-539
- [88] Yoshida S, Dhamrin M, Yoshida M, Uzum A, Itoh U, Tokuhisa H, Sekine S, Saitoh T, Kamisako K. Cost-effective front contact metalization by copper paste for screen-printed crystalline silicon solar cells. In: *Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition*; 2012; Frankfurt, Germany. pp. 1730-1732

