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NANOMETALLIC SILVER INKS FOR METALLIZATION OF ITO-COATED SILICON SOLAR CELLS: INFLUENCE OF ORGANIC COMPONENTS

Aline Gautrein[1], Christian Schmiga[1], Markus Glatthaar[1], Wolfgang Tremel[2] and Stefan W. Glunz[1]
[1]Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstraße 2, 79110 Freiburg, Germany
Phone: +49(0)761/4588-5489 Fax: +49(0)761/4588-9250 E-mail: aline.gautrein@ise.fraunhofer.de
[2]Johannes Gutenberg University, Institute of Inorganic and Analytical Chemistry, Duesbergweg 10-14, 55128 Mainz, Germany

ABSTRACT: Printed inks or pastes based on silver nanoparticles are promising alternatives for the metallization of temperature-sensitive silicon solar cells. We show that the sintering of silver nanoparticles strongly depends on the nature of the capping agent used to stabilize the particles during synthesis and in ink formulation. Particles capped by agents containing nitrogen as coordinative anchor group (between agent and silver surface) show poorer sintering under same conditions compared with particles capped by oxygen containing stabilizers. Polymers also hinder sintering more than shorter oligomers. In order to avoid unwanted spreading of the metal ink or paste during printing, the formulation has to be adjusted to the requirements given by the surface. If samples covered by a layer of indium tin oxide are stored in air, the surface energy rapidly decreases, dropping by around 30-50 % within one day. Thus, wettability and the work of adhesion also become poorer. This has to be taken into account by formulating inks for metallization on ITO layers.

Keywords: Low-temperature Metallization, Nanoparticles, ITO, Chemical Sintering, Silicon Solar Cells

1 INTRODUCTION

Due to their temperature sensitiveness, HIT (Heterojunction with Intrinsic Thin layer) and, for example, organic solar cells, still lack good metallization standards to be processed on mass production scale. Normally, cells of these concepts are contacted by ITO (Indium Tin Oxide) layers and a metal grid on top. For a low temperature metallization, nano-metal-based inks (particle size 1-100 nm) have become of interest. Although much effort has been spent in developing those inks during the last years [1, 2], they are still not commonly used in solar industry.

Great effort has been undertaken to lower the thermal sintering temperature by reducing particle size [3]. But particle size is not the only factor limiting the sintering temperature.

In this work we have analyzed the influence of organic components on the sintering behavior of silver nanoparticles in metal inks to allow a significant reduction of the temperature and to improve the electrical quality of the contacts at the same time.

Nanoparticle inks are often applied to a sample by printing methods based on ink technologies rather than pastes, like ink-jet printing. Inks contain a high amount of solvent and have very low viscosities. Therefor we have investigated the characteristics of ITO-covered surfaces towards solvents depending on the storage time in air to optimize the formulation of nanoparticle-based silver inks.

2 SILVER NANOPARTICLE SINTERING

Aim of the sintering process is to obtain a cohesive metal layer which should be as close in density to bulk metal as possible. The sintering process starts with the formation of *sintering necks* which connect the loose metal particles. Continuous sintering leads to sintering neck growth and densification of the metal layer.

Chemical sintering takes place according to the following process (Figure 1):

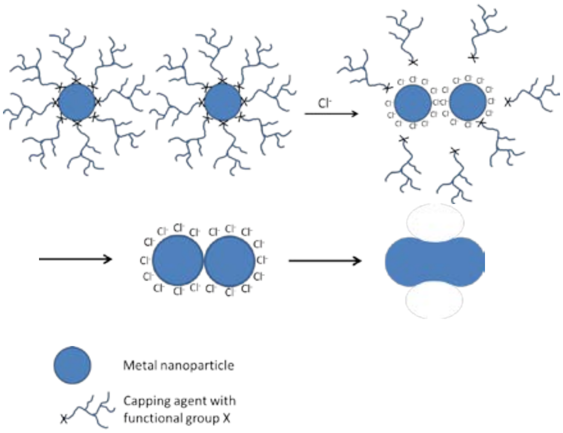


Figure 1: Schematic illustration of the chemical sintering process. Chlorine represents the sintering agent which can also be any other molecule known to have a strong interaction with the metal, e. g. other halides. X is a functional group interacting with the metal surface, e. g. carboxylic, amino or thiol groups. Scheme based on [4]

Metal nanoparticles have to be kept stabilized by so-called *capping agents* coordinated to the silver surface to prevent agglomeration and oxidation in the ink. For this purpose, normally bulky or electrostatic molecules are used. Bulky molecules provide a steric stabilization between the particles to keep them in a distance where van-der-Waals forces are not yet active and would lead to aggregation. Polymers are applicable for this purpose in organic solvents. For water-based systems, molecules with charged functional groups are chosen. Electrical repulsion keeps particles at distance. A combination of both effects is also possible if polymers with charged functional groups are used. This stabilization method is called *electrosteric*.

The capping agents interact via functional groups also called *anchor group* with the surfaces of the metal particles. The interaction takes place through heteroatoms like nitrogen, oxygen or sulfur. Those can, e. g., be found in carboxylic, amino or thiol groups. Halides are also known to interact very strongly with the surface of certain metals.

Sintering of the particles is triggered due to high surface forces if particles get into contact and grain boundary diffusion takes place [5, 6]. To remove the protecting capping agents from the metal surfaces one can either heat the particles up until the capping agents evaporate or decompose (high temperature sintering). Another way is to replace the coordinated anchor group of the capping agents by ions or molecules (*sintering agents*) with higher affinity to the metal surface or by using the principle of Le Chatelier and adding the sintering agents in excess. The capping agents loosen from the surface and diffuse away while the particles begin to sinter [4].

The sintering process continues until the energy reduction by neck formation between the particles equals the energy of grain boundary formation [5]. Further diffusion and sintering is only possible through external energy input (thermal, electrical, microwave, light-induced).

Integrity of the replacement of the capping agent is dependent on the strength of the interaction of the anchor group with the metal surface and the bulkiness of the organic group.

3 EXPERIMENTAL

In the course of this study, we investigated three metal inks with differently capped silver nanoparticles and four inks with diverse additives. Additives fulfill different tasks: They are utilized to adjust rheology, liquid surface tension, adhesion and other characteristics of the ink relevant for printability and shelf time. Additives are often polymers which remain in the printed pattern after ink curing. Therefore, a negative effect on the sintering behavior and thus on the electrical properties of the final contacts should be avoided.

The behavior of an ITO surface against unpolar and polar solvents depending on the storage time in air was investigated on planar and with random pyramids textured mono crystalline Si wafers coated with 70 nm thick sputtered ITO.

At Fraunhofer ISE, seven different ink formulations were tested. Variation parameters were capping agent covering the silver nanoparticles or organic additives, respectively.

Within this work we investigated the chemically triggered sintering behavior of three kinds of differently capped silver nanoparticles. Details of the used capping agents are given in table 1.

Furthermore we have analyzed the influence of four different additives, which fulfill different tasks in an ink or paste formulation (e.g. rheology additive, thickener, adhesion promoter). Details on the used additives are given in table 2.

The samples were prepared as follows:

20-50 wt% silver nanoparticles were dissolved in 50-80 wt% water/ethylene glycole (1:1). 50 µL of concentrated NH_4OH and eventually additives were added. The formulations were sonicated in an ultrasonic bath for 15 min and kept stirring until use.

The different inks were placed drop wise on surfaces of monocrystalline silicon wafers and dried on a hotplate at 150 C for 5 min. Afterwards the inks were chemically sintered in vapor of concentrated HCl within a distance of 2 cm for 10 s. The samples then were analyzed by scanning electron microscopy (SEM).

ITO for goniometer measurements was freshly sputtered on planar and alkaline textured mono Si wafers, respectively. Contact angles were measured with water (polar) and diiodmethan (DIM; unpolar). Measurements were done directly after deposition and several hours to weeks after storage in air.

Table 1: Details of Ag nanoparticles investigated in this work.

Particle type No.	Ø Particle size [nm]	Functional group	Organic group
1	20-50	N:	Polymer
2	10-20	NH_2	Oligomer
3	20	Carboxyl	Polymer

Table 2: Details of additives investigated in this study.

Additive	wt%	Functional group	Kind of additive
1	2.5	Carboxyl	Adhesion promoter
2	1	Hydroxy, Carboxyl	Electrical conductive
EC	3	Hydroxy	Binder
Gluten (not commonly used)	2	N, O	Binder

Surface tension measurements were performed with a Krüss Goniometer DSA25, surface energy was calculated applying the Owens-Wendt-Rabel- Kaelble-method [7] and was Hitachi SEM SU-70 used.

4. RESULTS AND DISCUSSION

4.1 Influence of capping agent

Figure 2 shows SEM images of the above described particles before and after chemical triggered sintering. As can be seen from these pictures, the sintering process is strongly dependent on the nature of the used capping agent. Particles of type 1 do not show any significant neck formation whereas particles of type 2 show the typical sintering necks. Bulky polymeric stabilizers provide not only a good protection against agglomeration but also against smaller particles (here chloride anions) to reach the metal surface as can be seen from Figure 2 comparing particles 1 and 2. The functional group in both cases is based on nitrogen but the polymeric organic group of particle 1 provides a far better steric hindrance.

Even more sintering necks and less visible grain boundaries are observed for particles of type 3. The comparison of particle 2 and 3 indicate that the enhanced sintering of particle 3 is due to the affinity of the carboxylic anchor group which is much weaker to the silver surface compared to the amine group. This is in accordance to the order of the relative silver – nonmetal element binding energy, E_B : E_B(Ag-N) > E_B(Ag-S) > E_B(Ag-O) [8]. As a conclusion, capping agents with functional groups including nitrogen (particle 1 and 2) are adsorbed more strongly to the silver surface than agents with functional groups containing oxygen (particle 3) as coordinator.

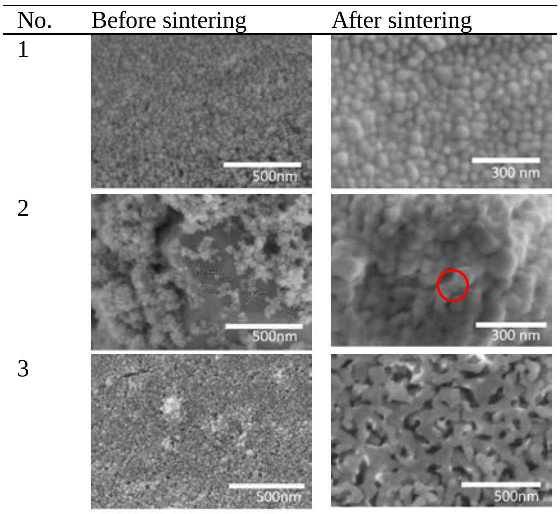
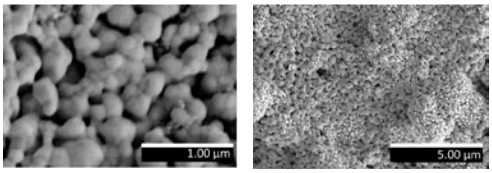


Figure 2: SEM pictures of Ag nanoparticles with different capping agents before (left column) and after (right column) chemically triggered sintering. Sintering neck is marked. Particle types according to table 1.

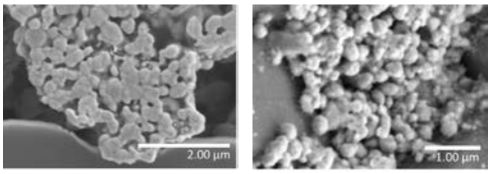
4.2 Influence of additives

Besides stabilized nanoparticles and solvents, inks and pastes normally contain additives to adjust, e. g., surface tension, viscosity, adhesion promoters and so on. Those additives potentially place between the particles after evaporation of the solvent and, thus, hinder or prevent sintering. We compared some common additives used in inks and pastes to investigate the impact of this effect by mixing inks using particle 3 and adding 1-3 wt% of additive. All additives are based on different polymers (see table 2).

The influence of additives on the self-sintering process is less significant than that of capping agents as demonstrated by the SEM pictures in figure 3. Note the different scales. Additives containing solely oxygen as potentially coordinative functional group do not influence the sintering process significantly (figure 3, table 2). If nitrogen containing functional groups are involved, like in the protein gluten, the sintering process is hindered. The steric structure of the polymers may also have an influence on this result. Different amounts of additives within narrow common limits have also been investigated but show no difference to the results displayed here. Nevertheless, much higher amounts could still have impact on the process.



Additiv 1 Additiv 2



Ethyl cellulose Gluten

Figure 3: SEM pictures of inks with different additives (see table 2) after drying at 200 °C for 5 min and sintering in HCl vapor.

4.3 Behavior of inks on ITO-coated surfaces

Indium tin oxide is known to adsorb water and oxygen on its surface if not stored under inert gas. This adsorption leads to a rapid decrease of surface energy which strongly influences the surfaces' behavior towards solvents [6, 8]. This is an important issue regarding ink formulation, wafer storage and the timescale for metallization after ITO deposition. By measuring the contact angle of different liquids, a calculation of the surface energy and a splitting in its polar dispersive part is accessible by the method according to Owens, Wendt, Rabel and Kaelble [9].

We used monocrystalline Si wafers with planar and with random pyramids textured surfaces covered by freshly deposited ITO layers as test samples for goniometer measurements. The planar wafers are used as a more ideal surface while the textured wafers represents a commonly used solar cell surface.

The behavior of the contact angle of water (polar) and diiodmethane (DIM, unipolar) were detected after wafer storage times ranging from some hours to several weeks. The samples were stored under ambient conditions in air between the measurements. Figure 4 and 5 show sample photographs of the different droplet behaviors due to changes of the surface energy of ITO. Figure 6 illustrates which angle is measured as contact angle.

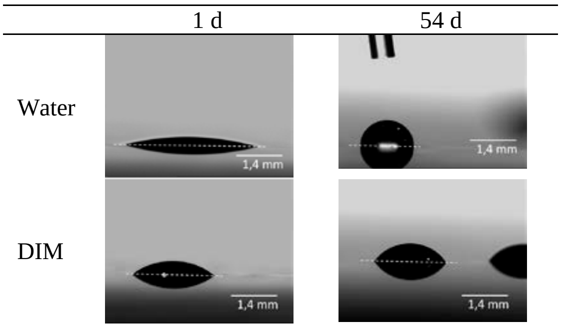


Figure 4: Goniometer pictures of water (top) and DIM (bottom) on by random pyramids textured Si wafers with ITO surface

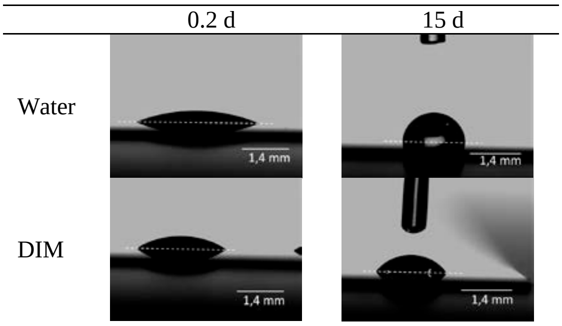


Figure 5: Measurement pictures of water (top) and DIM (bottom) on planar Si wafers with ITO surfaces

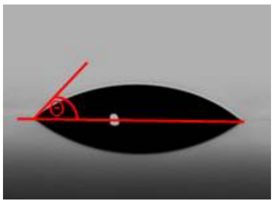


Figure 6: Illustration of measured contact angle.

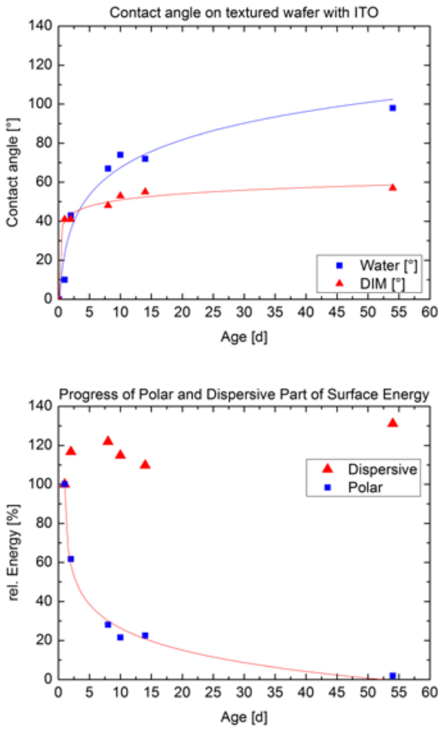


Figure 7: Development of contact angle (top) and polar and dispersive part of surface energy (down) on random pyramids textured and ITO-covered Si surfaces.

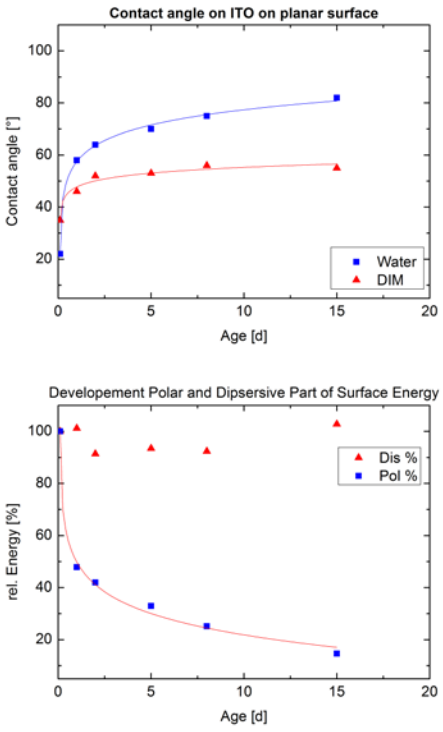


Figure 8: Development of contact angle (top) and polar and dispersive part of surface energy (down) on planar and ITO-covered Si surfaces.

Figures 4 to 8 show that the contact angles of water and DIM change dramatically within only one day of storage in air. The contact angle from water rises from 0° (total spreading on the surface which is not measurable and therefore not shown in figure 7) to almost 100° on a textured surface (Figure 4 and 7). A surface is considered as hydrophobic when the contact angle value is around 90°. At even higher values the surface is called superhydrophobic [6]. As can be seen in figure 7 particularly the polar part of the surface energy drops dramatically, which is in agreement with the adsorption of oxygen and water and, hence, the decrease in surface energy of ITO. Similar observations have been made on planar surfaces. The surface energy plays an important role regarding the adhesion and wettability: The higher the surface energy, the better adhesion and wettability [6] and, thus, interdependency between the ITO and metal surface, which might also lead to a better electrical contact between the materials.

5 SUMMARY AND CONCLUSION

Due to their low processing temperatures (depending on formulation and sintering process between 150 – 300 °C), inks and pastes based on nano-sized metal particles are of great interest for the metallization of temperature sensitive silicon solar cells, as HIT (Heterojunction with Intrinsic Thin layer) and organic cells.

We have demonstrated that the sintering of silver nanoparticles is strongly dependent on the kind of capping agent used to stabilize the particles during synthesis and ink formulation. Particles capped by agents containing nitrogen as coordinative anchor group (between agent and silver surface) show a poorer sintering behavior under same conditions compared with particles capped by oxygen containing stabilizers. Polymers also hinder sintering more than shorter oligomers.

We also observed, that nitrogen containing additives can hinder or completely suppress self-sintering of silver nanoparticles but the influence is less significant than of directly coordinated stabilizers.

Thus, to achieve most effective formation of sintering necks between particles at low temperatures (even room temperatures, for chemical sintering), care has to be taken in choosing the adequate stabilizing agent already at the beginning of the silver nanoparticle synthesis. Due to the different affinity of oxygen and nitrogen towards silver oxygen containing additives are more suitable for low temperature curing processes compared to nitrogen containing additives.

Investigations of the stability of ITO surfaces show that ITO changes its surface energy and, thus, its behavior towards solvents dramatically within even few hours after deposition if stored in air. This is important for the metallization of ITO by metallic inks. The metallization of Si surfaces covered by freshly deposited ITO layers may result in very large spreading of the ink on the wafer causing extremely broad contact lines with a very low aspect ratio. On the other hand if the metallization is applied after a period of some days or more, the wettability of ITO drops dramatically which could lead to low adhesion and/or bad contact formation between metal and ITO. As a consequence, ITO-covered solar cells should either be stored under inert gas or be further processed shortly after deposition. Ink formulation fitting to the ITO surface is obligatory. The addition of binders which makes the ink more viscous prevents the excessive spreading but would also make metallization by ink jet technique impossible. Metallization with more flexible techniques as aerosol jet or screen printing may be more advantageous.

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