Effects of Paste Composition and Sintering Process on Performance of Silver Paste for Silicon Solar Cells

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Abstract: In order to study the effects of composition ratios of silver paste and the sintering process on the properties of the silver film after sintering, the effects of different ratios of silver powders, glass powders and organic carrier in silver paste and different sintering temperatures and holding time on the adhesion force and square resistance of the silver film were studied through a series of experiments. The morphology of the sintered silver film was observed by SEM. The results show that the silver film sintered at 760℃ for 5 minutes has better properties after sintering when the ratio of silver powders, glass powders and organic carrier in silver paste is 80:5:15 and the silver powders are composed of spherical silver powders and flake silver powders at the ratio of 1:1. The adhesion force and square resistance of the silver film are 8.2 N and 5.6 mΩ/□, respectively.

Key words: silver paste; composition, sintering process; adhesion force; square resistance
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浆料组分及烧结工艺对太阳能电池银导电浆料性能的影响

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摘　要：为了研究银浆的组成比例和烧结过程对银膜烧结后性能的影响，通过一系列的实验研究了不同配比的银粉、玻璃粉和有机载体配制成银浆并在不同烧结温度和保温时间下烧结对银膜附着力和方阻的影响。烧结银膜的形态用扫描电镜观察。结果表明，当银粉、玻璃粉和有机载体在银浆中的配比为 80:5:15 且银粉由球形银粉和片状银粉按 1:1 的比例制备的银浆在 760℃烧结保温 5min 时性能较优。银膜的附着力和方阻分别为 8.2 N 和 5.6 mΩ/□。

关键词：银浆料；组分；烧结工艺；附着力；方阻

Silver conductive paste is a high technology electronic functional material. It has been widely used for the front electrode in solar cells because of its lower resistivity than other metals as well as the lowest cost among the noble metals in solar cells [1-2]. Silver conductive paste is mainly composed of three

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parts: silver powders, glass powders and organic carrier. Silver powders are widely used as conductive phase in the silver paste. It plays an important role on the conductive properties of the paste. Glass powders are widely used as adhesion binder, which could promote sintering of metal powders during sintering and provide the strength against warp. Organic carrier disperses the metal and glass powders to get good printing performance for silver paste [3-5]. Therefore, the content and characteristic of these components in the paste directly affect the performance of the silver conductive paste.

In this paper, the effects of different ratios of silver powders, glass powders and organic carrier in silver paste and different sintering temperatures and holding time on the adhesion force and square resistance of the silver film were studied.

1 Experimental

Firstly, the spherical silver powders (1.13 μm in average particle size) or flake silver powders (8.55 μm in average particle size) and the unleaded Bi_2O_3-B_2O_3-SiO_2 glass powders (3.1 μm in average particle size and 478.7℃ in transition temperature) were mixed with anhydrous ethanol. The evenly dispersed solid powders were prepared by stirring, ultrasonic dispersing and drying the mixture. Then the silver conductive paste was prepared by mixing and grinding the mixture consisting of the organic carrier and prepared solid powders with a three-roll rolling mill.

The silicon substrate was washed three times in deionized water and anhydrous ethanol respectively. Then the paste was printed onto the silicon substrate by screen printing process. The printed substrate was placed in air to flow flat about 10 minutes, and took into an oven for drying about 15 minutes, then sintered at a certain temperature. The adhesion force and square resistance of the silver film were measured after sintering.

Studying on the different ratios of silver powders, glass powders and organic carrier, the silver paste formula was according to Tab.1 and the ratio of spherical silver powders and flake silver powders was according to Tab.2.

Tab.1 The list of ingredients of silver paste

表 1 银浆组分表

Paste composition	Mass fraction/%				
Organic carrier	15%	15%	15%	15%	15%
Silver powders	84%	82%	80%	78%	76%
glass powders	1%	3%	5%	7%	9%

Tab.2 The ratio of spherical silver powders and flake silver powders

表 2 球形银粉与片状银粉配比表

Silver Powders	Mass fraction/%			
spherical silver powders	80	60	40	20
flake silver powders	0	20	40	60

2 Results and Discussion

2.1 Effect of the Composition Ratio of Silver Paste

For the composition ratio of silver paste, the silver powders and glass powders were mixed with organic carrier having the ratio ranging from 84/1/15 to 76/9/15 of silver powders /glass powders /organic carrier.

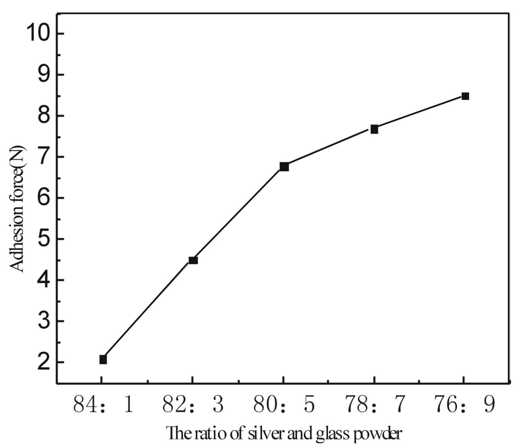

Fig.1 The influence of the composition ratio on the adhesion force of silver film

图 1 银膜组分配比对附着力的影响

The influence of the composition ratio of paste on the adhesion force is shown in Fig. 1. With the increase of the glass powder content, the adhesion force of the silver film and silicon substrate increased. When the glass powder content increased from 1% to 5%, the adhesion of silver film increased sharply. But when the glass powder content was more than 5%, the adhesion force increased slowly.

The major role of glass powders is to provide sufficient liquid glass phase for sintering. When glass powder content was low, the glass liquid content was insufficient to infiltrate the silver particles and the substrate adequately. The silver film and silicon substrate could not form good bonding, at the same time, the sintering densification of the silver film could be reduced, so the adhesion decreased. When the paste has a suitable composition ratio, such as 85/5/15 of silver powders, glass powders, and organic carrier, the silver particles and the substrate were wetted by the liquid phase glass. The bonding action between silver film and substrate was strengthened, so the adhesion had been further increased [6]. When the glass powder content continued to increase, the adhesion force of the silver film increased, but the increase was not obvious. With the increase of the liquid glass phase, the weld ability of silver film decreased because the excess glass liquid phase floated to the metal surface to form surface glaze, thus the adhesion force could not increased sharply.

The influence of the composition ratio of paste on the square resistance is shown in Fig.2.

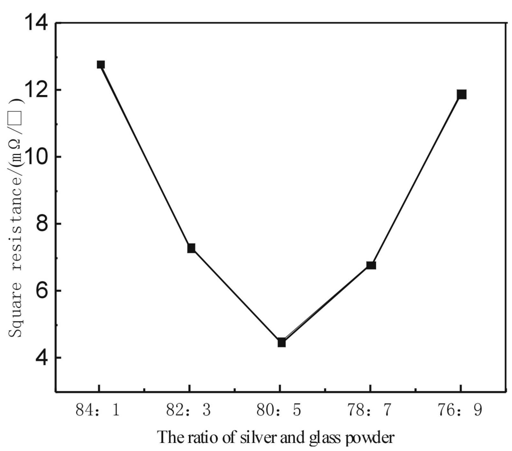

Fig.2 The influence of the composition ratio on the square resistance of silver film

图 2 银膜组分配比对方阻的影响

When the glass powder content was 1%~5%, the square resistance of silver film decreased. When the glass powders content was 5%, the square resistance got a minimum 4.5 mΩ/□ and the electrical conductivity was best. But when the glass powder content continued to increase, the square resistance increased.

When glass powder content was too low, the liquid glass content was insufficient. The silver powders could not be infiltrated and not spread on the substrate, so the driving force of densification was insufficient. The silver particles tended to grow along the vertical direction, and the weaker driving force was not enough to make all of the silver particles in conductive network. The contact between silver particles deteriorated, so the square resistance was big. When glass powder content was 5%, the amount of liquid glass phase was sufficient. Silver powders were effectively infiltrated and spread on the substrate, and the silver particles tended to grow along the horizontal direction, so the silver film had a compact structure and a good electric conductivity after sintering. When the glass powder content further increased, the silver powder content decreased relatively. The number of silver powder particles as the conductive phase in the paste significantly reduced. At the same time, the surplus glass powders would gather on the surface, and the contact spacing of silver particles became large. So the resistivity and the square resistance of the silver film increased [7].

Considering the influence of the composition ratio of paste on the square resistance and adhesion of silver film, when the composition ratio was 80/5/15 of silver powders, glass powders, and organic carrier, the adhesion and the square resistances of silver film were relatively better.

2.2 Effect of the ratio of spherical silver powders and flake silver powders

In the silver paste, the composition ratio was 80/5/15 of silver powders, glass powders, and organic carrier, and the ratio of spherical silver powders and flake silver powders was according to Tab.2.

Fig.3 shows the influence of the ratio of spherical silver powders and flake silver powders on the square resistance of silver film.

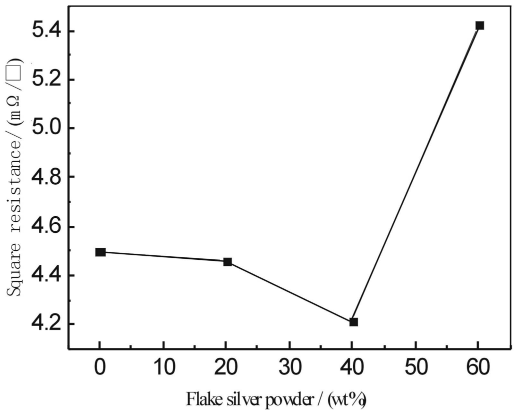

Fig.3 The influence of the ratio of spherical silver powders and flake silver powders on the square resistance of silver film

图 3 球形银粉与片状银粉配比对银膜方阻的影响

It can be seen from Fig.3, when the silver powders were pure spherical silver powders, the square resistance of silver film was 4.5 mΩ/□. With the addition of flake silver powders, the square resistance of silver film decreased. When the flake silver powder content was 40%, the square resistance had a minimum value. But when the flake silver powder content increased to 60%, the square resistance significantly increased. The reason for this change in the curve is: the conductive network composed of pure spherical silver particles at first, so the contact between the particles was the point contact. With the addition of flake silver powders, the contact between the conductive particles was the line and surface contact. The overlap occurred between the flake silver powders, and the spherical silver powders effectively filled the gap between the flake silver powders, so that the conductive capacity enhanced. When the content of spherical silver and flake silver had an appropriate proportion, the structure of the conductive network was closer, so the silver film achieved the optimum conductivity. But when the flake silver content was excessive, the resistance increased. This may be due to two reasons: Firstly, the printing effect of the paste with excessive flake silver reduced, resulting in that the connection between the silver particles was not close enough. Secondly, because the spherical silver powder content relatively less, so the connective effect between the flake silver powder particles decreased, resulting in that the conductive effect decreased.

The SEM image of the sintered silver films corresponding to 0%, 40% and 60% flake silver powder content are shown in Fig.4.

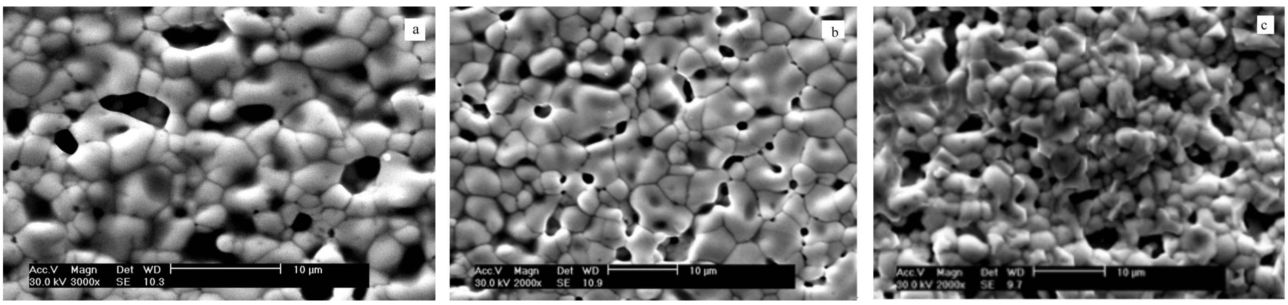

Fig.4 SEM image of the silver film with different contents of flake silver powders (a) pure spherical silver powders, (b)40% flake silver powders and (c)60% flake silver powders

图 4 (a)纯球形、(b)40%片状和(c) 60%片状三种银粉的银膜 SEM 图

From images of Fig.4, it is more clearly observed that the structure of the silver film was relatively dense when the flake silver powders mixed with spherical silver powders in proper proportion，it helps to reduce the resistivity. The silver film with pure spherical silver powders had slightly larger gap between the silver particles after sintering. This may be because when the conductive phase of paste was pure spherical silver powders, the contact between conductive particles mainly was point contact, so the contact area between silver powder particles was less and conductive chain in the silver film was easy to disconnect，as shown in Fig.4(a). Adding a certain amount of flake silver powders, the morphology of sintered silver film would be changed. The flake silver powders had a certain deformation and contraction during sintering process. The spherical silver powders as conductive bridge dispersed between the different flake silver powder layers. So the conductive network was denser and the conductivity of the conductive chain was better, as shown in Fig.4(b). But when flake silver powders were overmuch, the flake silver powders accumulated after large deformation and had agglomeration phenomenon. Meanwhile, the lack of spherical silver in the connection between the layers, the conductive performance was not ideal, as shown in Fig.4(c).

2.3 Effect of Sintering Temperature

As can be seen in Fig.5, when the sintering temperature elevated from 700℃ to 760℃, the adhesion force increased rapidly. After more than 760℃, the adhesion force decreased.

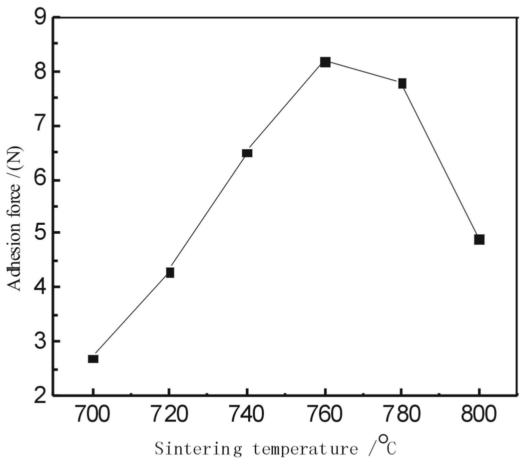

Fig.5 The influence of sintering temperature on the adhesion force of silver film

图 5 烧结温度对银膜附着力的影响

It is the reason that lower sintering temperature could not melt the glass powders sufficiently; therefore it was unable to effectively wet the substrate to get good adhesion force. With the sintering temperature rising, the glass powders could be melted sufficiently. The surface tension between the liquid and the solid substance reduced gradually, so the wetting ability of the silver paste could be better. The silver powders and the substance could be wetted effectively by glass liquid phase, so the silver film had good adhesion force after sintering. However, when the sintering temperature was too high, the viscosity of glass liquid decreased and the silver powders could deposit [8]. That would reduce the glass powder content on the contact area, and the weld ability of silver film would greatly reduce because the surface glaze occurred, so that the adhesion force reduced after sintering.

The influence of sintering temperature on the square resistance of silver film is shown in Fig.6.

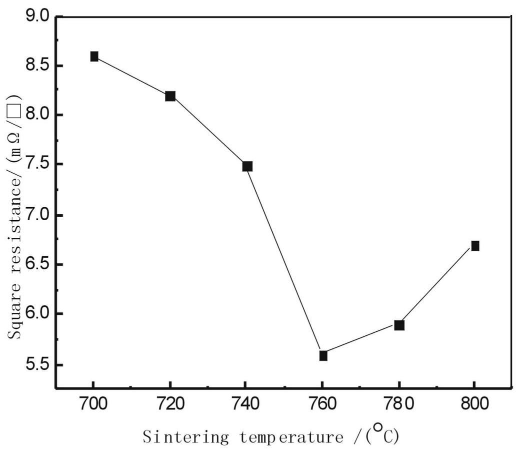

Fig.6 The influence of sintering temperature on the square resistance of silver film

图 6 烧结温度对银膜方阻的影响

When the sintering temperature increased from 700℃ to 760℃, the square resistance reduced from 8.6 mΩ /□ to minimum value 5.6 mΩ/□. But after 760℃, the square resistance increased gradually.

With the increase in sintering temperature, the amount of glass liquid increased gradually and the silver particles were wetted effectively by glass liquid. The contraction of the inorganic binder made silver particles drag in the horizontal direction, so the conductive phases had good contact to form a dense conductive network and the conductivity of the silver film got better, as shown in Fig.7. But when the sintering temperature reached 800℃, the viscosity of the glass liquid reduced, resulting in an uneven distribution of conducting phase and inorganic binder phase, so that the connection between the silver particles was not dense enough and the conductivity of the silver film reduced[9].

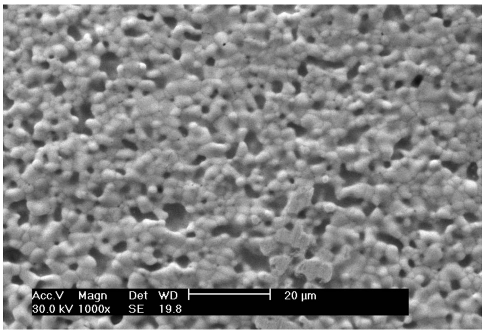

Fig.7 SEM image of the silver film sintered at 760℃

图 7 760℃烧结银膜 SEM 图片

2.4 Effect of Holding Time

Fig.8 and Fig.9 show the effects of holding time on the adhesion force and the square resistance of silver film.

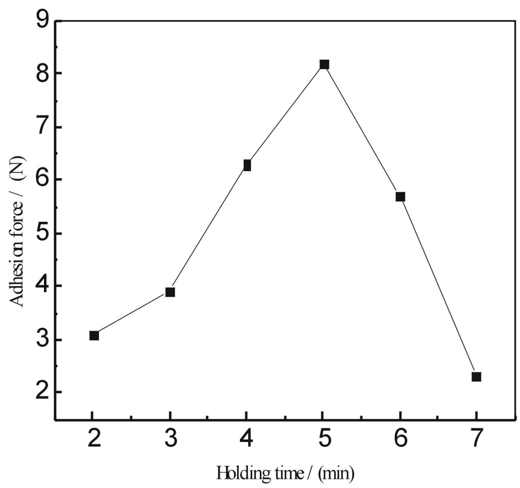

Fig.8 The influence of holding time on the adhesion force of silver film sintered at 760℃

图 8 银膜 760℃烧结时保温时间对附着力的影响

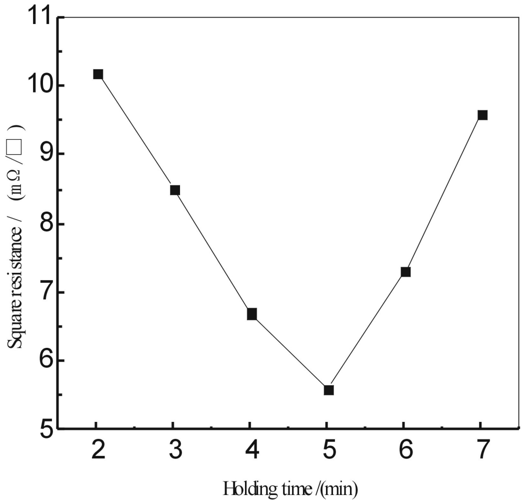

Fig.9 The influence of holding time on the square resistance of the silver film sintered at 760℃

图 9 银膜 760℃烧结时保温时间对方阻的影响

From the two curves, they obviously reflect that the silver film had better performance when the holding time was 5 minutes. During the sintering process of silver film, when the holding time was from 2 minutes to 5 minutes, the adhesion of silver film gradually increased, meanwhile, the square resistance gradually decreased. But when the holding time was more than 5 minutes, the conductivity and the adhesion of silver film all decreased.When the holding time was not enough, the silver powders and the substrate could not be infiltrated sufficiently by glass liquid, resulting in that the adhesion and the compactness of silver film were not enough. But if the holding time was too long, the viscosity of glass liquid decreased. The diffusion was excessive and the surface glaze formed, so the adhesion force and solder ability reduced, meanwhile, the square resistance decreased. Therefore, the holding time should not be too long during the sintering process [6, 10].

Considering the influence of holding time on the square resistance and adhesion force of silver film, when the holding time was 5 minutes, the silver film could obtain better electric conductivity and higher adhesion force. The structure of the silver film was compact, and the void age was small. The glass phase completely wrapped silver particles, and a regular conductive network formed in silver film, as shown in Fig.10.

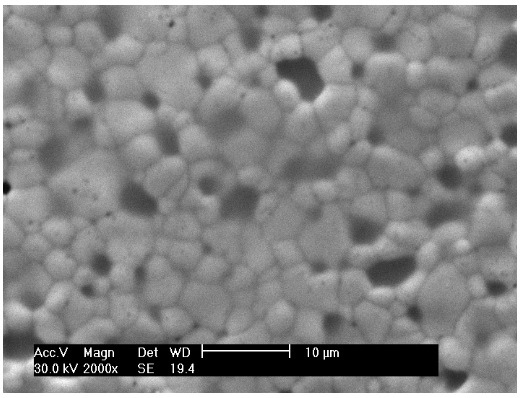

Fig.10 SEM image of silver film sintered at 760℃ for 5 min

图 10 银膜在 760℃烧结保温 5minSEM 图

3 Conclusion

The effects of different ratios of silver powders, glass powders and organic carrier in silver paste and different sintering temperatures and holding time on the adhesion force and square resistance of the silver film were studied. The results show that the silver film has better properties after sintering when the ratio of silver powders, glass powders and organic carrier in silver paste is 80:5:15 and the silver powders are composed of spherical silver powders and silver flake silvers at the ratio of 1:1. The adhesion force and square resistance of the silver film are 8.2 N and 5.6 mΩ/□, respectively, when the sintering temperature is 760℃ and the holding time is 5 minutes.

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