Research of nano silver alloy pasteto solar cell

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Abstract. From theory and experiment, the method toimprove the performance of silver paste was explored. Through the analysis about the SEM images to the electrode contact section of the crystal silicon solar cell, the different contact modes and resistance calculation methods of the metal paste and silicon were verified. Through the resistance calculation, consideringthe different oxide and silver silicon contact alloy characteristics, two kinds of additive compositions were found that which may have good performance in alloy paste of the solar cell.

1. Introduction

Over the world, more than 85% crystalline silicon solar cells adopt the silver paste as raw material of thick film screen printing production. As precious metal material, silver`s high market price makes it difficult to meet the needs of our use. Thus, systematic studying crystalline silicon solar cell emitter, decreasing the contact resistance of crystalline silicon solar cells are important to improve the efficiency of crystalline silicon solar cells and decrease the cost of PV power generation.

Due to the diversity about material resistance and alloy properties, the crystal silicon solar cell has contact resistance on the contact surface of the emitter and the silver electrode. As one of the most important functional structures of crystalline silicon solar cells, the electrical properties of Ag-Si contact affect the performance of solar cells. There are a lot of researches on the electrical properties of Ag-Si contact, mainly about the contact conduction mode, the carrier transport mechanism, the contact resistance and so on[1-4].

In this letter, the method to improve the performance of silver paste was explored. Through the calculation and analysis of the electrode contact section SEM images of the crystal silicon solar cell, the different contact modes and resistance calculation methods of the metal paste and silicon were verified. Through the resistance calculation, considered the different oxide and silver silicon contact alloy characteristics, two kinds of additive compositions were found that which may have good performance in alloy paste of the solar cell.

This letter will be helpful to the production of crystalline silicon solar cell, reasonably reduce the resistance of silver silicon contact, improve the efficiency of the crystalline silicon solar cell. At the same time, it can also helps to optimize the ratio of material in silver alloy paste, reduce the cost of PV power generation.

2. Metal paste and silicon electric contact model

2.1. Metal paste and silicon contact carrier conduction mechanism
Due to the excellent electrical properties, rich crust reserves and so on, Tin is widely used in electrical contact materials field. At the same time, Sn-Si alloy has a good performance in anti-oxidation, anti corrosion, anti welding, reduce resistance and other aspects. Therefore, the electrical contact properties of tin and silicon will be discussed further in this letter.

In order to facilitate the research, we made the 156*156mm Sn electrode crystal silicon solar cell tablet from "the Yellow River" factory as the sample.

In order to directly study the situation about the Sn-Si contact, we made a series of SEM images to the contact area of the sample, as shown in figure 1.
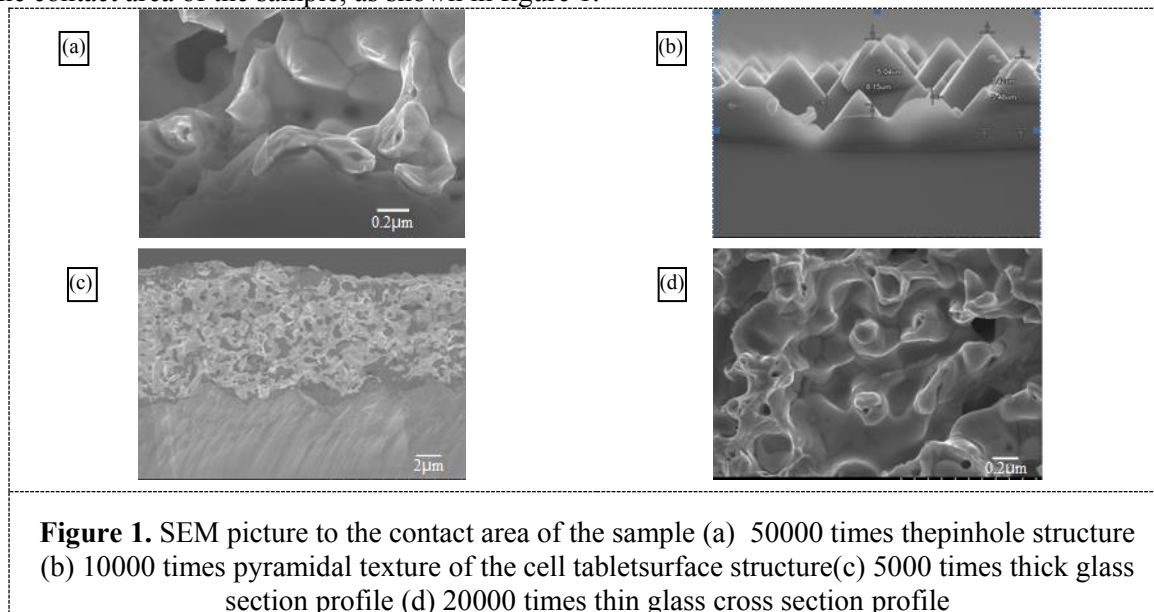

Figure 1. SEM picture to the contact area of the sample (a) 50000 times thepinhole structure (b) 10000 times pyramidal texture of the cell tabletsurface structure(c) 5000 times thick glass section profile (d) 20000 times thin glass cross section profile

According to the SEM images, three main modes of Sn-Si contact can be found. Similar to the three contact modes of screen printed silver paste and silicon contact proposed by Song-Yeu Tsai and Ching-Hsi Lin in 1982 [5].Samples in Sn-Si are mainly performed three kinds of electrical contact mode, the carrier also transfers through the three kinds of modes:

First, the carrier is transported through the direct contact with silicon. This is the direct contact mode of Sn-Si.[6-9]

Second, the carrier is indirectly tunneling through the thin glass layer between the Sn and Si. This is the Sn-thin glass layer-Si indirect contact mode. According to the concept of Tsai Ching-Hsi, Lin Song-Yeu, this model should be the main mode of the screen printing paste and the silicon electric contact carrier[5].

Third, the carrier can be transported directly to the electrode through the thick glass layer which is with the not continuous silicon. This is a Sn-thick glass layer (with a discontinuous metal particle)-Si indirect contact. This contact resistance is very large, so it is not conducive to improve the PV efficiency of solar cells [10], [11].

The three contact modes between metal and silicon are formed during the sintering process, so the sintering process will directly affect the properties of the metal and silicon electrical contact.

Based on the existing research and literature, we can calculate the contact resistance of the three contact modes.

Among them, the contact resistance of Sn-Si direct contact mode can be calculated by the classical contact theory; the contact resistance of Sn-thin glass layer-Si mode can be calculated by the formula of tunneling resistance at low voltage; the contact resistance of Sn-thick glass layer (with a

discontinuous metal particle)-Si indirect contact mode can be calculated through the calculation of the electrical conductivity. The electrical resistivity and conductivity under three contact modes can be deduced from Eqs. (1)~(3). [5-9]

$$\rho_c \cong (\frac{1}{E_{00}})\exp(qV_{b0}/E_{00})$$

(1)

$$\rho_{c2} = \frac{h^2 d}{e}(2m\phi)^{1/2}\exp[\frac{4\pi d}{h}(2m\phi)^{1/2}]$$

(2)

$$\delta = 2e^2 d^2 \nu_p N(E_F)\exp(-2\gamma d - w/\kappa T)$$

(3)

After that, the total contact resistance can be obtained combined with the contact area ratio of the three modes. (According to the relevant literature research, the contact area ratio of the three contact modes is about 3:3:1. [5], [7])

The calculated value total resistance of Sn-Si sample is $R = 6.86 \times 10^{-5} m\Omega$, which is similar to the actual measured value. It proved that the calculation method of the total resistance applied.

3. Study on a new type of positive silver paste additives

3.1. The selection of additives
Because the effect of additives on the positive silver paste`s property has multiple ways, there will be a variety of factors should be considered in the selection of additives. Due to the electric performance is relatively independent and the interface resistance calculation method are analyzed, the additives is selected mainly based on the electrical properties here.

According to the electrical contact barrier between metal and P type doped silicon, we selects the element as the additive with the low electric contact barrier. Under the condition that the crystal structure and the properties of the alloy are not considered, the ohmic contact resistance formed between the lower electric contact barrier is lower. This judgment can be directly proved by common sense: the electrical contact barrier of the daily known good electrical properties metal will be lower than it of the bad electrical properties metal [7]. In addition, also have to consider the scarcity degree of elements and the market price of oxide. Like gold and other similar elements, although the electrical contact barrier is low, the output around the world is not enough or the price is too high. This makes it not conducive to reduce the cost of solar cell production. Finally, in order to facilitate the test, we also have to consider if there is the relevant oxide particle product with high purity, suitable size and shape. Otherwise it will be difficult to carry out the research. Finally, 9 metal oxide products are selected as the modified additive component. They are $SnO_2, PbO, Nb_2O_5, ZrO_2, TiO_2, CeO_2, PdO, Er_2O_3, RuO_2.$

3.2. Contact resistance calculation
In order to further explore their electrical properties as well as a reference for the experimental verification, this letter calculates the expected contact resistance of the nine elements.

Although the elements are different, the electrical contact is still mainly by direct contact, Sn-thin glass layer-Si indirect contact, Sn-thick glass(with discontinuous tin particles)-Si indirect contact modes. Therefore, the tin silicon contact model can be directly applied to the calculation of ohmic contact resistance of other elements.

According to the electrical contact barrier between different metal and P type doped silicon, the total contact resistance of different metal electrode crystal silicon solar cell can be calculated by the method mentioned earlier. The results are showed in table 1.

Table 1. Predicted total contact resistance of different metal electrode

	($m\Omega$)		($m\Omega$)		($m\Omega$)		($m\Omega$)
Sn	$6.89*10^{-5}$	Pb	10.78	Nb	12.25	Zr	20.96
Ti	15.70	Ce	153.38	Pd	$1.171*10^{-28}$	Er	152.24
Ru	$1.189*10^{-15}$						

According to the calculation results, the relationship between the total contact resistance of different metal electrode crystal and the electrical contact barrier between different metal and P can be embodied by Matlab, as shown in figure 2.
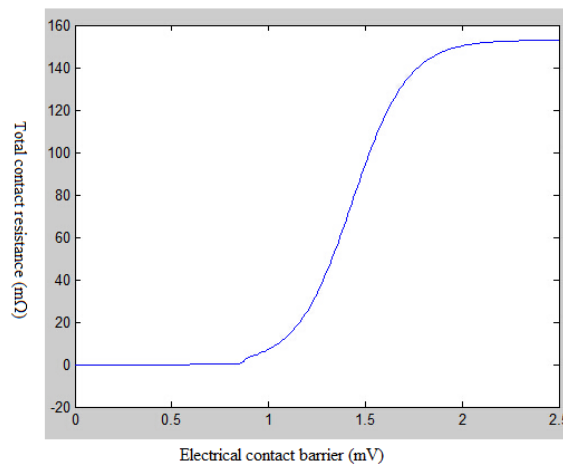

Figure 2. Relationship between contact resistance and electric contact potential barrierbetween the metal and the P type doped silicon

In the figure, the contact resistance is mainly generated when the electric contact barrier is in the range of [5], [10]. It can be learned that, as long as the electrical contact barrier is maintained at less than 1, the total contact resistance and other electrical properties will not generate a large float.

According to the calculated results, the electrical properties of several elements in accordance with the order of Pd, Ru, Sn, Pb, Nb, Ti, Zr, Er, Ce, respectively, the electrical properties of the order decreased. Pd, Ru, Sn, as the best electrical properties of several kinds of metal, can be considered.
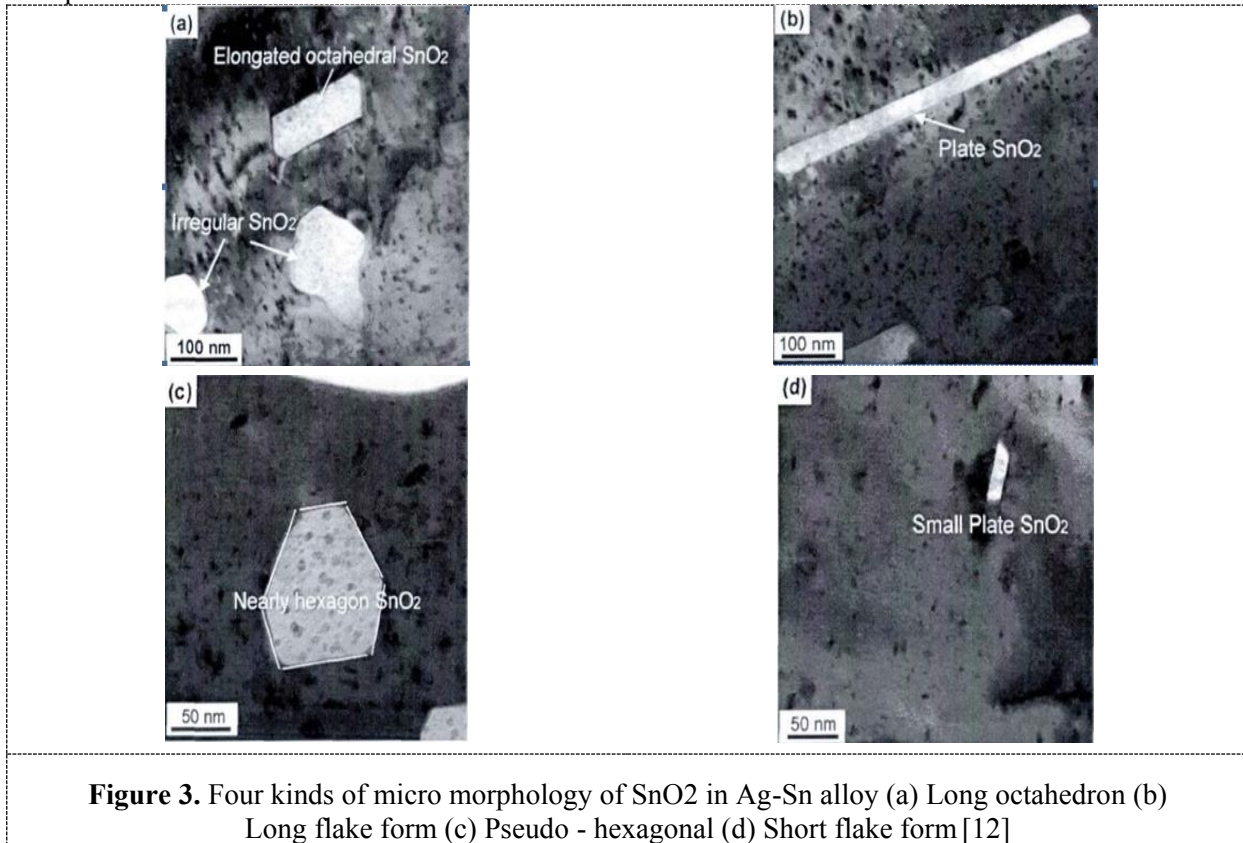
3.3. Analysis of crystal properties of alloy
The electrical properties of metals have been discussed above. However, this is a discussion on the premise of not considering the different crystal structure and the special alloy phase. In order to make a more detailed study, further microstructure and properties of the alloys was analyzed.

3.3.1. Ag/Sn alloy At present, there are many researches on the properties of silver tin alloy. Four kinds of micro morphology of SnO2 in Ag-Sn alloy are showed in figure 3.[12]

SnO_2particles have four different morphologies. Each kind of SnO2 particle will form different kind of alloy. With the addition of different metal, sintering process and temperature, the properties of the alloy are also different. Therefore, there are many researches on the Ag-Tin electrical contact materials.

At the present stage, the research is mainly focused on the improvement of metal oxide additives in Ag-Tin alloy. In order to improve the characteristics of alloys in oxidation, corrosion resistance, welding resistance and so on. The appearance of these characteristics is closely related to the crystal

structure of the alloy and the contact interface. The appearance of these characteristics is closely related to the crystal structure of the alloy and the contact interface. For example, some of the alloy phase will only form at a fixed temperature. So in the sintering process, it must reach or exceed the temperature and maintain for a certain time.

Figure 3. Four kinds of micro morphology of SnO2 in Ag-Sn alloy (a) Long octahedron (b) Long flake form (c) Pseudo - hexagonal (d) Short flake form [12]

   3.3.2. Ag/Ru alloy Compared with Sn and other electrical contact material, Ru has no special place in resistance and anti welding etc. However, Ru will form a special alloy with Ag[13]. The micro morphology photo of Ag-Ru alloy are showed in figure 4.

Figure 4. Micro morphology photo of Ag-Ru alloy with different magnification times (a)2000 (b) 1000 [13]
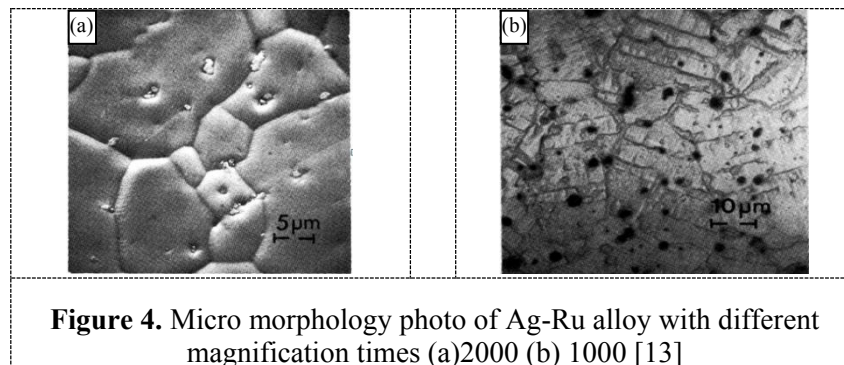
   The contact resistance of the Ag-Ru alloy is very small, even in the humid environment the alloy is rusty and oxidized. At the same time, even if the contact force is very small, the contact resistance can still be kept in a small value, as shown in figure 5. [14]

Figure5. The relationship between contact resistance and contact force in the humid environment after 21 hours [14]
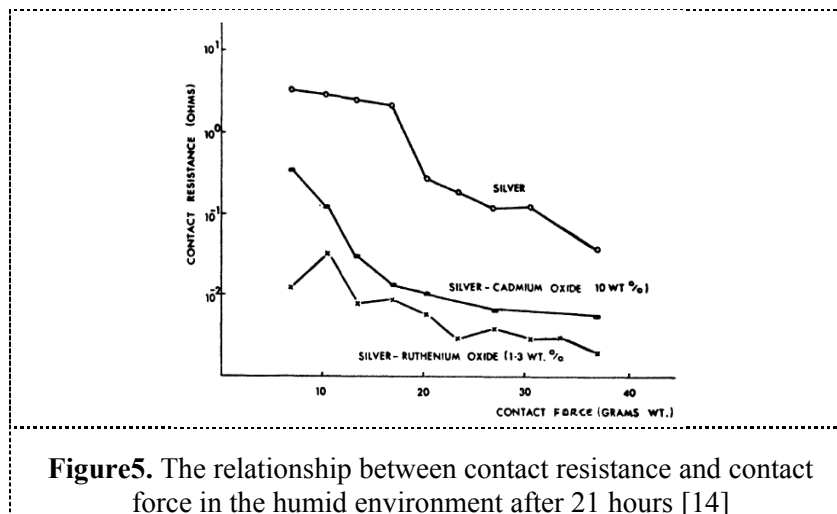
This special property of Ag-Ru alloy has special value in actual production. The contact resistance of most electric contact material will increase rapidly because of rust [14].It caused that a lot of electrode contacts will be difficult to use, or cannot be used when they are rusted. Some of them can even caused some danger. As a result, the service life and reliability of these electrical contacts will be reduced, affecting the quality of the products. If the electrical contact material is made of Ag-Ru alloy, the electrical properties of the material will be kept in a damp, rusty and little contact force condition [14]. This will greatly extend the life, the scope of application and the reliability of the electrical contact.

4. Conclusions and outlook

Based on the analysis of the conductive mechanism of crystalline silicon solar cells, the effects of different additions on the properties of nano silver alloy pastes were discussed.

Based on the calculation of resistance and the characteristics analysis about the alloy, it is concluded that Ag-Sn and Ag-Ru alloy may have good performance in alloy paste of the solar cell. However, the actual production and detection of the alloy paste were deficient about the two kinds of additives. In addition, the influence of sintering process is not discussed in this letter either. The next step is to test actual performance about those two kinks of additives in alloy paste of the solar cell, and to discuss the effect of sintering process on the performance.

With the rapid development of PV industry, the demand for silver paste, which has excellent electrical conductivity, printing adaptability and aging resistance, is growing rapidly. Therefore, it is necessary to continue optimizing the alloy paste of solar cells. It will be helpful to reduce the consumption of Ag and further reduce the cost of PV power generation.

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