Technological route and characteristics of home - built Ag, Ag/Cu, and Ag/Ni ohmic conductor pastes

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Abstract

The current research reports the preparation and fabrication of the silver paste conductor which is employed as a soldering material for electro – optical components ohmic interconnections. The prepared paste possesses electrical characteristics identical to the ohmic connectors as its observable from resistance – temperature variation. Moreover, the I – V characteristics obeys Ohm's law and this dependency was further confirmed by the nearly constant capacitance measurements with voltage and frequency. A noticeable improvement in electrical conductivity, compared to the pure silver paste sample, was noted for samples prepared by mixing predetermined weight ratios of brass and copper. Furthermore, stability of electrical resistance with time was investigated and the resistance was approximately constant.

Key words

Electro – optical Silver paste
Ohmic conductor soldering material

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المسلك التكنولوجي وخصائص عجينة (الفضة، الفضة/نحاس، والفضة/نيكل) الموصلة الأومية المحلية الصنع

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الخلاصة:

يصف البحث الحالي تحضير و تصنيع عجينة التوصيل الأومي – عجينة الفضة- والمستخدم كـ مادة لحام لعمل توصيلات أومـية للمكونات الكهرو – بصرية الدقيقة وخاصة المتحسسات البصرية (الكواشف). تمتلك عجينة الفضة المحضرة خصائص كهربائية متطابقة مع نتائج آلية التوصيل الكهربائي للموصلات الأومية من خلال تغير المقاومة مع درجة الحرارة وأن خصائص التيار – الفولتية تخضع لقانون أوم. تم ملاحظة تحسن ملحوظ وزيادة في التوصيلية الكهربائية للعينات المحضرة من خلطات وزنية محددة لمادتي النحاس والبراص مقارنة بعجينة الفضة النقية. علاوة على ذلك، تمتلك العينات مقاومة كهربائية ذات أستقرارية عالية ثابتة تقريباً مع الزمن.

Introduction

The fabrication and development of electro – optical components, of which detectors are an example, require the use of silver paste soldering material of as small ohmic resistance (i.e., highest conductivity) as possible between the detector electrodes and the electrical connection wires [1].

Normally, electrical interconnects other than silver paste exhibit considerable impedance to the detected electrical

signal as the latter signal is being transported from the detector electrodes to the external electronic circuits [2]. The Ohmic interconnect (connector) represents an important characteristic feature and has a great influence on the electro –
optical properties of semiconductor junctions. It may be defined as the connection of semiconductor to metal such that the connection has the smallest possible resistance as well as its voltage – current characteristics obey Ohm's law [3].

Theory and evaluation

The ohmic connector represents a unique and influential parameter on the electro – optical characteristics of semiconductor junctions. The ohmic connection interconnects a metal and a semiconductor with the least possible resistance. Furthermore, its I – V characteristics obey Ohm's low.

The total resistance R_t of a semiconductor junction is estimated by the formula [1, 2]:

$$\mathbf{R_t = R_{sc} + 2R_c \dots\dots\dots (1)}$$

Where $\mathbf{R_c}$ and $\mathbf{R_{sc}}$ are the connector and the semiconductor junction resistance respectively.

For the connection to be ohmic $\mathbf{R_c}$ has to be so minute ($\mathbf{R_c \cong 0}$). Thus, equation 1 becomes:

$$\mathbf{R_t \cong R_{sc}}$$

Technological Route of Fabrication

To prepare the ohmic interconnect paste, the chemical technological route has been adopted [4, 5]. This route involves the using of the following materials to prepare the paste:

1. Cellulose nitrate.
2. Silver rod.
3. Nitric acid.
4. Silver nitrate.

1. Cellulose is considered one of natural polymers. It contains thousands of glucose molecules and each molecule in turn involves three types of alcohol. The cellulose is transformed to nitrate by the chemical reaction of hydroxide group with nitric acid. In this reaction, the cellulose is diluted in ethyl acetate and adding a plasticizing material like camphor to produce cellulose nitric varnish.

The cellulose nitrate atom includes 10.5 – 11 % nitrogen and the amount of nitrogen determines, in advance, the properties of the cellulose nitrate. Thus, when the nitrogen content is 10 %, the cellulose nitrate is plastic and when it is 11 %, the cellulose nitrate is varnish while 12 – 13.8 % nitrogen results in a stony cellulose nitrate. In general, the varnish layer is transparent and fast drying.

The cellulose nitrate varnish was prepared via the reaction between the cotton and the mixture of concentrated sulfuric and nitric acids in which the nitric acid is introduced into the cellulose resulting in the formation of a material that is dissolved by organic solvents such as ethyl acetate and acetone of a specific concentration. After that, a plasticizing material is added to the varnish to get the desired paint which gives the required specifications like age, dryness time. A time – proof specification material was added to the varnish. This material possesses very high conductivity and does not react with the varnish in order to make it a conductor [5].

1-A 99.99 % purity silver rods have been employed to prepare a powder of the conductor by analyzing the metal (silver) in diluted nitric acid (50 %) and heating the solution followed by introducing high purity (99.99 %) copper rods. Once the powder is formed, it is thoroughly washed with water and then well grinded such that the resulted grain size should be no more than $\mathbf{50\ \mu m}$. This is an essential step to guarantee the homogeneity between powder grains and the varnish. Thus the electrical conductivity will be the same at all conductor points. The above chemical reactions are described as follow:

$$\mathbf{Ag + 2HNO_3 \rightarrow AgNO_3 + H_2O + NO_2 \uparrow}$$

(SILVER NITRATE)

$$2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag \downarrow$$
$$Ag + N.C(nitro\ cellulose) \rightarrow silverpaste$$

The silver is mixed at a ratio of 70 % with the varnish to get the desired conducting varnish.

1. Silver nitrate was used to get silver precipitate. This is accomplished by dissolving silver nitrate in distilled water and then introducing the copper rods. After that the precipitant powder is washed with water and dried. The dried powder is then grinded as in the previous procedure to get grains of approximate size of **50 μm**. Silver nitrate is preferable compared to silver rods in view of the possibility of getting very pure powder at minimum cost [4, 5, 6].

Various samples were prepared by mixing silver at a ratio of 60 % with brass and copper at a ratio of 40 % each. The resulted powder samples were mixed with varnish to produce different pastes [7].

Experimental work and Measurements

Conductivity measurement: Clean glass substrates have first been prepared and washed with water for about 15 minutes. Shortly after that, the glass substrates were introduced into the ultrasonic bath cleaning system. Then substrates were washed with pure alcohol and to dry them, they are put in an oven at a temperature of 100 ^oC for approximately 15 seconds. A special solution was exploited to clean the glass substrates and once again they were washed with alcohol and dried in a 100 – ^oC temperature oven for 10 seconds. On the cleaned glass substrates**,** a 1 – μm thin film was deposited utilizing the thermal vacuum coating system. The deposition (evaporation) parameters were as follows:

Coating chamber pressure: 10^{-5} mbar,

sample (glass substrate) holder temperature: 100 ^oC.

Rate of deposition of Al: 1μm/min.

A spiral tungsten evaporation canister was made use of. The geometrical dimensions of the prepared samples on which the Al electrodes were deposited are illustrated in figure 1.The electrical conductivity (resistivity) of the pure silver paste was compared with other pastes in which their

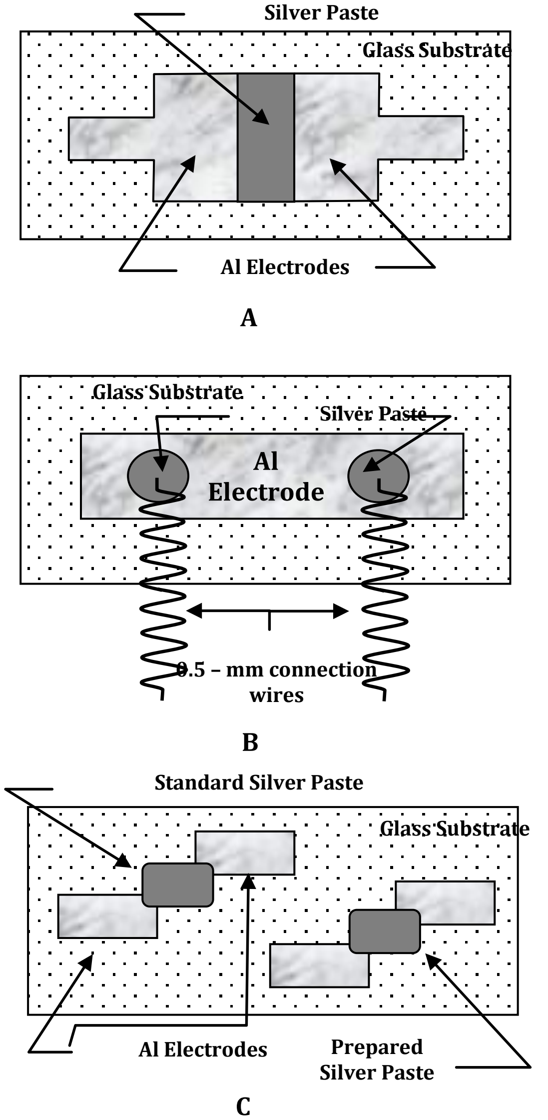

Fig. 1: Ohmic silver paste interconnector in different Al electrode configurations.

Table 1: Variation of resistance with temperature, electrodes – connector of figure 1 – A and 1-C

Temperature °C	Resistance Ω Standard	Resistance Ω Prepared
20	13.8	14.0
30	14.5	17.6
40	14.3	17.2
50	15.2	21.3
60	18.0	25.5
70	19.8	22.0
80	39.0	41.0

Table 2: Variation of resistance with temperature, electrodes – connector of figure 1 - B

Temp. ºC	Resistance copper/ nickel Ω	Resistance copper Ω	Resistance pure Ω
30	3.60	27.28	88.6
35	3.72	25.95	90.0
40	3.92	26.60	89.4
45	3.95	27.08	89.84
50	4.00	27.5	86.7
60	3.96	31.9	88.1
70	4.01	33.8	98.16
80	5.23	48.5	112
90	8.15	57.8	113.6
100	14.18	65.45	117

conductivity was increased by the addition of brass and copper metals. Moreover, the effect of temperature on conductivity was scrutinized, tables 1, 2.

1. Ohmic conductivity measurement a current – voltage characteristics: an HP – multimeter was used to measure the prepared sample resistance as in figures 1 – A and 1 - B.

In figure 1 – C, a comparison between the conductivity (i.e., electrical resistance) of the prepared silver paste and a standard one was done for Al – electrodes separation of 3 mm and at room temperature. For the latter test the silver paste resistance was estimated to be 14 **Ω** compared to 13.8 **Ω** of the standard paste. On the other hand, a I – V characteristics of a silicon sample has been performed and the conducted measurements revealed that the characteristics are linear and obey Ohm's low.

2. Influence of temperature on the electrical resistance T – R: in this test, illustrated in figure 2, both the prepared and standard silver paste samples are introduced between the Al electrodes and a 0.5 – mm connection wires were interconnected between their corresponding Al electrode and a 0.5 connection wire. The samples were put in a Heraeus type thermal oven in which the temperature can be varied from about 250 ºC down to -100ºC. The effect of temperature on paste interconnect's resistance was examined using an HP multimeter.

3. Capacitance – voltage c - v measurement: the c – v measurements of the prepared samples were performed for both the pure silver paste and the one of the improved conductivity due to the addition of brass and copper. Thus, the ohmic characteristics were further confirmed.

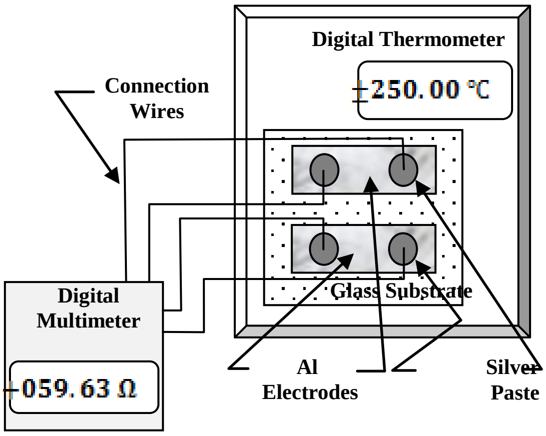

Fig. 2: variation of resistanc with temperature

Results

The resistance of the pure ohmic silver paste on the Al electrode prepared via thermal vacuum coating system was identical to that of the standard silver paste at the measuring conditions, (table 1). The variation of resistance with temperature (table 2) reveals that the prepeared ohmic

Table 3: Variation of silver paste capacitance with the applied voltage and frequency

Frequency MHz	Applied Voltage volt	Capacitance nF					
		Silver past pure		Copper/nickel copper		Copper	
		Forward	reversed	forward	reversed	forward	Reversed
0.5	0 - 1	92.9	90.47	0.74×10^{-3}	1.2×10^{-3}	1.66	85.6
1	0 - 1	6×10^{-3}	0.75×10^{-3}	6.1×10^{-3}	1.3	1.5	1.5

silver paste has similar electrical characteristics to that of the ohmic conductors.

The current – voltage characteristics of the sample silver paste demonstrate a linear dependence, i.e., it obeys Ohm's law. The capacitance measurements were approximately constant with the applied voltage and frequency variations, during which no noticeable change in junction capacitance were observed. Thus, the mechanism of the ohmic connectivity of prepared silver paste was further confirmed.

The silver paste samples demonstrated high stability of resistance with time as illustrated in the resistance – time stability measurement of figure 3 in which the resistance of the sample is practically steady.

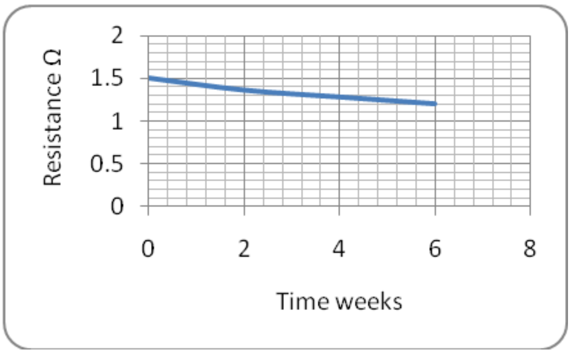

Fig.3: variation of silver paste ohmic resistance with time

Furthermore, the paste possessed the same very low capacitance due to changing the bias voltage polarity, table 3.

An obvious improved electrical ohmic connectivity, as compared to the pure ohmic interconnect, was noticed for the samples prepared by mixing pure silver with predetermined weight ratios of brass and copper.

Conclusions

The paper reports the preparation of an inexpensive, reliable silver paste interconnect that can be employed in electrical connections of semiconductor junctions. The efficiency of the paste is comparable to the standard (about 95 – 97 %) and may be introduced in the fabrication of the ohmic connections of the various electro – optic components.

The current silver paste doesn't require the use of thermal oven to solidify as it's the case for the standard paste. The latter feature is so important due to the fact that the temperature at which the standard paste solidifies is about 200 ^{o}C and most semiconductor devices are vulnerable at this temperature.

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