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Conductive Silver Patterns on Polyimide Substrate by using Alkali Paint Modification – Ion Exchange – Reduction (AIR) Process via low requirements mask technology

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A new type of alkali paint was formulated, which can be roller coated on polyimide film to prepare silver patterns by using AIR process via low requirements mask technology. Moreover, we successfully fabricate a double-sided silver pattern on polyimide substrate at one step for the first time.

Conductive patterns have variety of application, such as in radio frequency identification (RFID) electronic tags, molded interconnect devices (MID) and integrated circuits (IC). For this reason, the preparation of conductive patterns is playing an important role in the microelectronics industry. Conductive patterns mainly refer to copper, silver, nickel and so on. As we know, silver has excellent conductivity and anti-oxidation properties. Conventional methods of preparing silver patterns include silver nanoparticle ink, metal precursor ink and ion-exchange self-metallization. Silver nanoparticle ink contains silver nanoparticles, dispersants which can make silver nanoparticles stable, solvent and other additives. Sintering process is necessary after printing silver nanoparticle ink in order to obtain the conductive silver layer, which can make dispersants decompose and facilitate solvent volatilize. The previous sintering temperature is high which is generally over 200 ℃ [1], which is a kind of restriction for many substrates whose glass temperature Tg is below 200℃. To reduce sintering temperature and improve the stability of silver nanoparticle ink at the same time, researchers have attempted to adopt different silver organic precursors to formulate metal precursor ink which can be directly decomposed at a certain temperature [2], reduced by fractional reduction method [3] or by direct inspired reduction under some conditions (heat treatment [4,5] or laser irradiation [6]). Silver organic precursors have a lower decomposition temperature but worse conversion rate and solubility in water compared with silver inorganic precursors (silver nitrate or silver oxide). Hence many researchers have successfully prepared inorganic metal precursor ink by introducing silver inorganic precursors (silver nitrate or silver oxide) which can also be reduced by fractional reduction method [7] or by direct inspired reduction under some conditions [8,9].

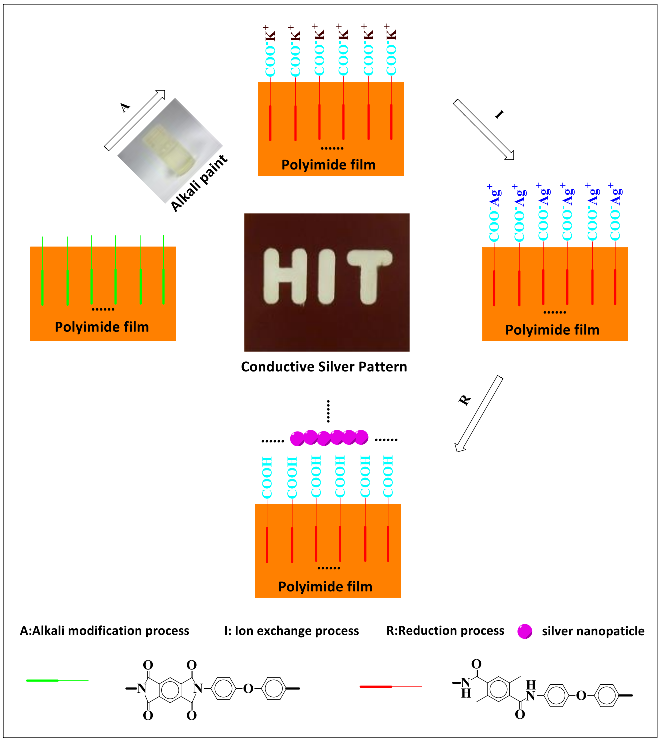

Fig. 1. The principle scheme of fabricating silver patterns on polyimide substrate by Alkali paint modification-Ion exchange-Reduction (AIR) process (HIT is the abbreviation of Harbin Institute of Technology).

Ion exchange Self-metallization is proposed as a kind of silver metallization method on polyimide film. This method has been attracting considerable researchers' interest [10-12] because the adhesion and conductivity of the silver coating is good. Many researchers prepared all kinds of silver patterns by using this method and variety of printing technology such as micro-contact printing, inkjet-printing, screen printing, and so on [13-15]. These methods are all using mask and mask are all immersed in high concentration alkali solution. It puts forward higher requirements to mask and moreover the above mask are not easy to be wiped out by mechanical methods. At the same time, the above mask is easy to remain on polyimide film. Recognizing these problems, we have developed a unique method of preparing conductive silver patterns on polyimide substrate, using an innovatively designed alkali paint coupled with low requirements mask technology. The principle scheme of fabricating silver patterns on polyimide substrate by Alkali Paint Modification- Ion Exchange–Reduction (AIR) Process is shown in Fig 1.

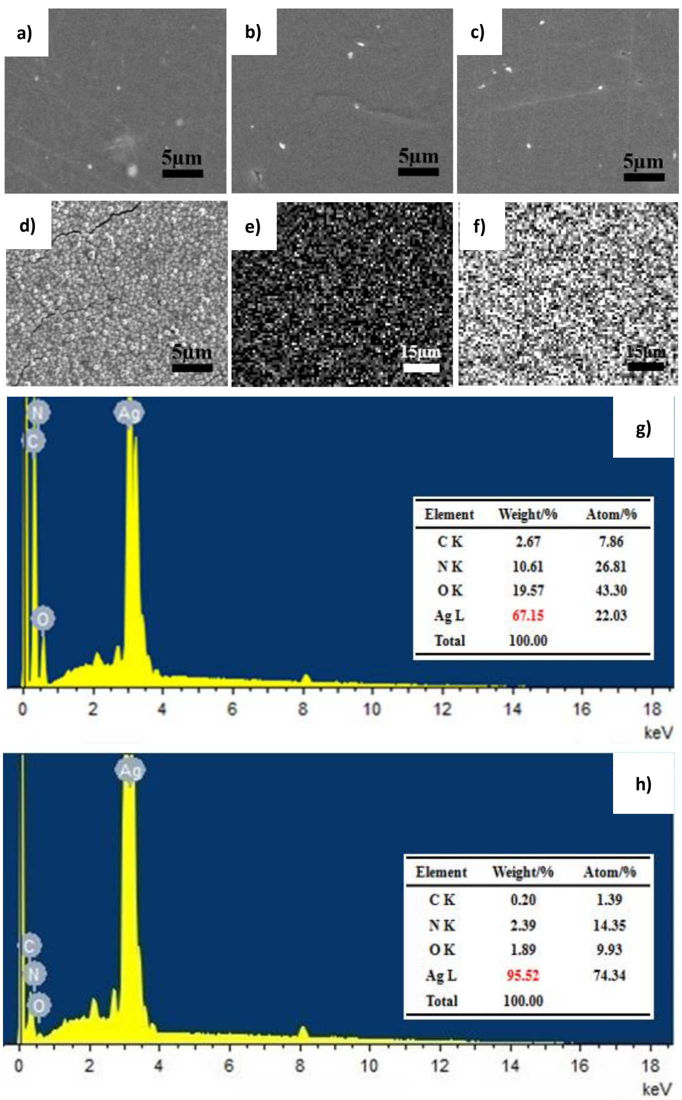

Fig. 2. SEM images (a~e) of fabricating circular(Φ3cm) silver pattern on polyimide film during AIR process and the EDS test results of the silver pattern layer after Ion exchange process and Reduction process. (a) Polyimide patterned film after removing oil, (b) Polyimide patterned film after Alkali modification process, (c) Patterned polyimide film after Ion exchange process, (d) Polyimide film after AIR process, (e) EDS surface scanning image of silver element (the white dot) on Polyimide patterned film after Ion exchange process, (f) EDS surface scans image of silver element (the white dot) on patterned polyimide film after AIR process. (g) EDS of patterned polyimide film after Ion exchange process, (h) EDS of patterned polyimide film after AIR process.

To investigate the surface microstructures throughout the whole process described in the experimental methods section by low requirements mask technology coupled with a roller-coating technique. After polyimide patterned film was wiped by ethyl alcohol (CP) in order to remove the oil, the surface of polyimide film is flat (Fig. 2a). The microstructure of the polyimide film after alkali modification process demonstrates clear micro cracks (Fig. 2b), and the amide bond is hydrolyzed to carboxyl potassium under high concentration of alkaline conditions (Fig1). After the Ion exchange process (Fig. 2c), a large number of silver particles are observed on the surface of polyimide patterned film (Fig. 2d). However, the micro cracks are still found on the surface of silver patterned polyimide film.

At last, The EDS spectrum (Fig. 2h) shows that the silver patterned film is obtained finally and the content of silver element becomes more after AIR process (95.52wt%, Fig.1h-inset table) compared with after Ion-exchange process (67.15wt%,Fig.2g-inset table). At the same time, the EDS surface scanning image of silver element(the white dot) demonstrates that the white spots of Polyimide patterned film after AIR process (Fig. 2f) become denser compared with after Ion exchange process (Fig. 2e), which confirms the content of silver element increases. The above results show that the silver particles may have obvious aggregation during Reduction process.

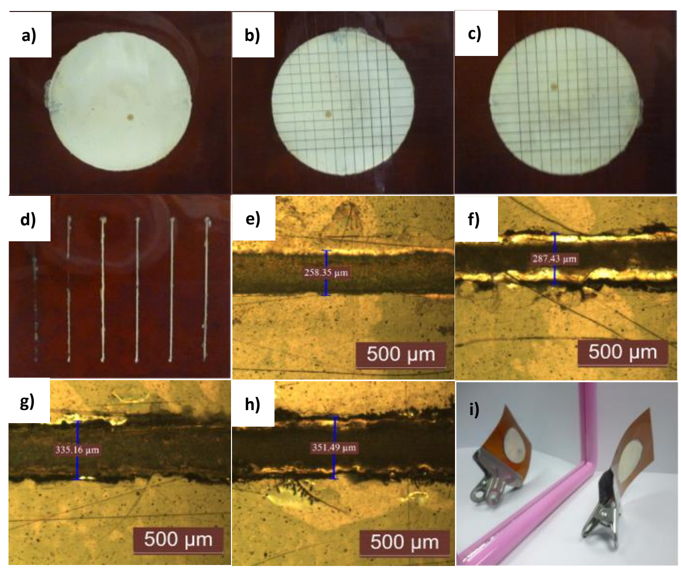

Fig. 3. Preparation and performance characterization of variety of silver patterns on polyimide film after AIR process. (a) The digital photograph of circular (Φ3cm) silver pattern on polyimide film, (b) The digital photograph of

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circular (Φ3cm) silver pattern on polyimide film crossed by Cross-Cut Tester (2cm space), (c) The digital photograph of circular (Φ3cm) silver pattern on polyimide film crossed by Cross-Cut Tester (2cm space) after the 3M600 tape test (Note: Binding force test level is evaluated as 0 level according to GB/T 9286-1998 standard), (d) The digital photograph of line array silver pattern on polyimide film (the line width according to computer settings is 0.001mm, 0.025mm, 0.050mm, 0.075mm, 0.100mm, 0.125mm from left to right successively, the line length is 3cm), (e)~(h) the silver line width measurement of 0.050mm, 0.075mm, 0.100mm, 0.125mm line from left to right successively by Metallographic microscope (the test direction is transverse), (i) The digital photograph of double-sided circular(Φ3cm) silver pattern on polyimide film.

Then all kinds of silver patterns including circular (Φ3cm) silver pattern (Fig. 3a), "HIT" characters silver pattern (Fig 1) and line array silver pattern (Fig. 3d) were fabricated on polyimide film by AIR process. The results of Cross-Cut test and the 3M 600 tape test (Fig 3b and Fig 3c) show that there is a good adhesion between the silver layer and polyimide film. The line array silver pattern shows that when the line width according to computer settings is 0.001mm and 0.025mm, silver wire becomes discontinuous. The silver line width measurement of 0.050mm, 0.075mm, 0.100mm, 0.125mm line from left to right successively by Metallographic microscope (the test direction is transverse) are 258.35μm, 287.43μm, 335.16μm, 351.49μm (Fig 3e~h). The thickness of the silver layer of the circular (Φ3cm) silver pattern is about 0.51μm (d). The sheet resistance of the silver layer of the circular (Φ3cm) silver pattern is about 147.09mΩ ($R_□$). The resistivity of the silver layer of the circular (Φ3cm) silver pattern is 7.5μΩ•cm ($\rho = R_□ \times d$), and the conductivity is 21.2% of the bulk silver value (20℃). Excitingly, double-sided circular (Φ3cm) silver pattern on polyimide substrate was fabricated at one step by AIR process for the first time (Fig 3i).

In conclusion, a new type of alkali paint was prepared and used to fabricate successfully variety of conductive silver patterns on polyimide film by AIR process coupled with low requirements mask technology and roller-coating technique. Low requirements mask technology employs the common PVC mask and patterned PVC mask covered with polyacrylate pressure-sensitive adhesive which were removed easily and no residue. The roller-coating technique is a kind of technology close to industrialization. Excitingly, double-sided silver pattern on polyimide substrate was printed once at the same time by AIR process for the first time, which would lay the foundation for the preparation of double-sided flexible PCB in the future.Although the definition of the silver pattern fabricated by AIR method has been improved a lot compared with the traditional ion exchange selfmetallization method (Fig S1). However, the definition of the silver pattern is not high owing to osmosis of alkali and need to be improved further.

Experimental

Preparation of alkali paint

1) firstly 10 g deionized water, 20 g glycerin (AR) and 10 g anhydrous ethanol (AR) were successively weighed into a beaker, mixed and stirred evenly;
2) 20 g potassium hydroxide was weighed into another beaker;
3) The breaker of 2) was cooled by the cool water ahead of time, then mixed liquid of 1) was poured into 2), the beaker mouth was sealed rapidly with plastic wrap at the same time. Finally the mixture was stirred until potassium hydroxide was completely dissolved. When the temperature of the mixture reduced to room temperature, the alkali paint was prepared completely at last.

Mask is a kind of commercial polyvinyl chloride (PVC) mask covered by polyacrylate pressure sensitive adhesive which is usually used in advertising design production. In this paper, we choose PVC mask as a kind of low requirements mask to be studied. Patterned PVC mask can be obtained by mechanical engraving using universal engraving machine on this kind of PVC mask. PVC mask covered polyacrylate pressure sensitive adhesive was pasted on polyimide film by manual operation, removed easily by manual operation and no any residue can exist on the surface of polyimide film.

Fabricating silver patterns by AIR process via mask technology

1) the double-sided of polyimide film was wiped by ethyl alcohol (CP) in order to remove the oil, and then cleaned with water, cleaned with deionized water, and dried successively; the bright side of polyimide film was covered with patterned PVC mask, the rest of polyimide film was covered with PVC mask.
2) Alkali modification process: the bright side of polyimide film was roller-coated with the alkali paint by roller bar (8#) and dried under 65℃ for 10 min, and then washed clean with deionized water;
3) Ion exchange process: the above polyimide film was immersed in 0.1 M silver nitrate (AR) solution at room temperature for 30 min, and then was cleaned with deionized water;
4) Reduction process: the aforementioned polyimide film was immersed in 0.25 M ascorbic acid (AR) solution at room temperature for 10 min. Then the above polyimide film was cleaned with deionized water and blow-dried by the cold wind. At last, after tearing off the PVC mask and patterned PVC mask by manual operation, the polyimide whose bright-side printed with the silver pattern was prepared completely.

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Notes and references

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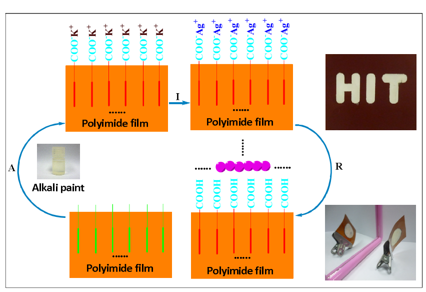
We fabricate conductive single-side and double-sided silver patterns at one step by using AIR process via low requirements mask technology.



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