WITHDRAWN: Preparation of Silver Nanopowders and Its Application in Low Temperature Electrically Conductive Adhesive

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Abstract

Printable electrically conductive adhesive with high electrical conductivity and good mechanical properties has wide application prospect in electronic device. In order to explore new conductive fillers of interconnecting materials in electronic circuit and electronic packaging industries, silver nanopowders were prepared by DC arc plasma method with high pure. The silver nanopowders present a spherical structure, the particle's diameter range from 15 to 220 nm. In this paper, a high performance electrically conductive adhesive (ECA) was prepared. This ECA was fabricated by mixing silver nanopowders with epoxy resin and was screen-printed to a required shape. It was found that the ECA can be solidified through a low temperature sintering method in the air at 150 ℃ for 10 min. The electrical and mechanical of above ECA were investigated and characterized. The ECA filled with 75% silver nanopowders exhibits excellent performances, including high electrical conductivity (9.5×10^{-4} Ω·cm), high bonding strength (8.3 MPa). Based on the performance characteristics, the ECA applications in flexible printed electrodes and interconnecting materials are demonstrated.

1 Introduction

The Sn-Pb solder widely used in the traditional electronic packaging industry has exposed its disadvantages, such as too high solder welding temperature, easy to damage devices, too low line resolution, unfriendly to the environment and so on. The ECA has the advantages of environmentally friendly, less processing steps, narrow processing width and low temperature, which has attracted widespread attention [1–4]. The ECA is the main substitute for Sn-Pb solder and has become an indispensable new material in the electronic industry [5–7]. In order to enhance the adhesion and conductivity of ECA, conductive fillers, curing agents, diluents and promoters are added to the matrix resin. Conductive fillers provide conductive ability for ECA, so the performance of fillers can greatly affect the conductive performance of the composites. The conductive fillers of ECA are mainly include metal powders, graphite, carbon nanotubes [8–14]. The metal filler has good conductivity and usually include silver, copper, gold, chromium, nickel and lead-free alloy. The silver is widely used because of its good electrical conductivity, moderate price and strong antioxidant properties. Compared with micron scale silver powder, silver nanopowder has the characteristics of large specific surface area, high surface energy and high chemical reaction activity [15–22]. At present, high dispersion silver nanopowder is mainly prepared by electrolysis, spray pyrolysis, chemical reduction and DC arc plasma evaporation under atmosphere protection. The silver nanopowder prepared by vacuum DC arc plasma method has high purity and high yield. Matrix resin plays a role in providing polymer skeleton and bonding strength in ECA. Matrix resin mainly includes epoxy resin, polyimide, phenolic resin, silicone and thermoplastic. Epoxy resin has strong bonding force, stable performance, high transparency corrosion resistance. Although ECA have many advantages and are widely used, compared with metal solders, they are still in the immature stage of technology, and there are many technical problems to be solved, such as poor mechanical properties, large volume resistivity, poor thermal conductivity, etc. This paper mainly studies

the mechanical and electrical properties of isotropic conductive adhesive to narrow the gap between isotropic conductive adhesive and metal solder.

In this experiment, highly dispersed and nearly spherical silver nanopowder was prepared by vacuum DC arc plasma method. It was applied to isotropic conductive adhesive, printed on different substrate, and then cured at low temperature to prepare conductor. The effects of conductive filler content on conductor resistivity and shear strength were systematically studied.

2 Experimental

2.1 Materials

Ag bulk and copper sheets were supplied by Nanjing Jinyan Nanotechnology Co. Ltd. (China). Epoxy resin (E51) was purchased from Sinopharm Chemical Reagent Co., Ltd. The PET film was supplied by Shanghai Xiangsu Wujin Co. Ltd. (China).

2.2 Characterization

The morphology of the prepared powders was measured by transmission electron microscope (TEM)(FEI Tecnai G20, USA). The Ag nanopowders were analyzed by X-ray diffractometer (XRD) (ARL XTR, Switzerland). The resistance of the conductor was analyzed by RTS-8 four-point probe instrument (Gang Zhou, China). The scanning electron microscopy (SEM) (Su8010, Japan) was used to investigate the morphology of the conductor. The electronic universal testing machine (CMT2503, MTS Systems Corporation) was used to calculate the adhesion strength of the cured adhesive joint, and the tensile rate was 5 mm/min according to GB/T1040-1992.

2.3 Ag nanopowder preparation

Ag nanopowder is prepared by high vacuum three gun DC arc plasma equipment. The experimental process parameters are: cathode current 440A, inflation pressure 0104 MPa, hydrogen argon ratio 2/3. The equipment diagram is shown in Fig. 1.

2.4 ECA preparation

In order to explore ECA, the organic carrier was prepared and selected by measuring its bonding strength and the resistivity of the conductor sheet. The final organic carrier included 100g E51 epoxy resin, 50g triethanolamine, 15g acetone, 15g active diluent, 5g dibutyl phthalate and 10g anhydride. The Ag nanopowder and the organic carrier were mechanically stirred for 5 min, and then placed in the ultrasonic cleaning machine for 10 min. The conductive filler and the organic carrier were evenly mixed to form ECA. The ECA was evenly coated on the PET film by screen printing to obtain a square thin layer (20mm (length) ×20mm (width) ×0.2mm (thicknesses)). The ECA was printed between two metal sheets and the joint area between the two metal sheets was 12.5mm×10 mm. The prepared samples were placed in the thermal aging box and were cured at 150℃ for 10 minutes.

The Fig. 2(a) and 2(b) show that the images of school badge are clearly distinguishable on the PET substrate. The Fig. 2(a) shows flat state and Fig. 2(b) shows the intense curling state. Conductive patterns show the flexibility and printability of the ECA.

3 Results And Discussion

3.1 Formation and microstructure of silver nanopowder

In the experiment, high vacuum three gun DC arc plasma evaporation equipment was used to prepare Ag nanopowder. The cleaned pure silver ingot was putted in a crucible. The vacuum chamber was evacuated by a vacuum pump after sealing the equipment, and was filled with hydrogen and argon. Adjusting the distance between the two arcs to an appropriate distance, high-temperature plasma can be generated between the two poles. The high-temperature plasma rapidly heated the silver ingot, and the silver was evaporated to form steam. The circulating gas brought the Ag steam to the powder receiving chamber. H_2 dissociated in the arc to form high-temperature active H. The active H jet entered the melt and cooled in the Ag melt to form H_2. A large number of hydrogen bubbles overflowed from the inside to the outside of the Ag melt. It was observed in the test that the Ag melt had a stable somersault phenomenon when the amount of hydrogen was small, and the somersault phenomenon was more obvious when the amount of hydrogen increased. When the hydrogen argon ratio reached 2/3, the Ag melt boiled violently. Therefore, it can be considered that the addition of hydrogen made the metal transition from general evaporation to boiling evaporation, and the evaporation rate was greatly improved. The Ag vapor collided with argon molecules, rapidly lost energy, cooled, nucleated and grown, and finally condensed and deposited to form loose powders. Finally, the equipment was turned off and cooled, and the Ag powders can be collected at room temperature.

Figure 3 shows the TEM diagrams of silver nanopowders at different magnification. Due to the large surface tension of silver nanopowders, the particles attract each other and arrange in a chain shape. The particle size of silver nanopowders in Figure 3(a) is analyzed by PCI software. Figure 3(b) gives a magnified image for Figure 3(a). The results show that the average particle size of silver nanopowders is 55nm, and the particle size distribution is between 15~220nm.

Figure 4 shows the XRD spectrum of the Ag nanopowder, which is almost the same as the standard card of 04-0783. There are no diffraction peaks of other substances, which shows that the purity of silver powder is high. The diffraction peaks with 2θ angles at 38.1°, 44.3°, 64.4°, 77.4° belong to (111), (200), (220) and (311) crystalline planes of Ag, respectively. From the position of the diffraction peak, the cell parameter is a=b=C=4.0828 nm. Compared with the standard card 04-0783 parameter a=b=C=4.0862 nm, the cell volume is reduced by 0.083%. Compared with larger bulk silver materials, silver nanopowder is subjected to greater surface tension, which compresses the particles and shrinks their lattice.

3.2 Electrical resistivity and shear strength of the as cured ECA

As shown in Fig. 5, with the increase of silver nanopowder content, the resistance first decreased significantly and then decreased slightly. When the mass fraction of Ag is 55%, the resistance value is larger, which is $1.55\times10^{-2}\Omega\cdot$cm. When the mass fraction increases to 75%, the resistivity of the conductive adhesive decreases sharply to $9.5\times10^{-4}\Omega\cdot$cm, the conductivity increases sharply. According to the percolation theory, it can be determined that the percolation threshold of ECA is 75%. The high content of silver nanopowder builds an efficient conductive network in the epoxy resin matrix to provide current and heat conduction paths. However, too high content leads to poor rheological properties and the silver nanopowder cannot be evenly mixed with the resin matrix.

It can be seen from Fig. 6 that the selected E51 epoxy resin has large shear strength, which is mainly due to the relatively large number of flexible groups in its molecular chain. The shear strength of ECA decreased with the increase of silver nanopowder content. After increasing the content of silver nanopowder, the cohesive energy density of the epoxy resin system is reduced and the mechanical properties of the resin system are reduced. The shear strength for the ECA with 75% silver nanopowder is 8.3 MPa. Excessive addition of silver nanopowder will reduce the crosslinking degree of epoxy resin, make the resin system brittle and poor mechanical properties. It is remarkable that the shear strength of the ECA declines significantly at the content of silver nanopowder over 75%. Meanwhile, the ECA with the 75% silver nanopowders shows an excellent electrical conductivity. Thus, the 75% silver nanopowders as conductive filler is recommended. The results show that the ECA prepared by screen printing method have well conductive and tensile properties.

3.3 Morphology and chemical structure of conductive polymer film

The SEM image of the as cured ECA conductive polymer film filled with 75% silver fillers is shown in Fig. 7. The silver nanopowders can be clearly identified. Fig. 7 shows that the nanopowders exhibit uniform distribution, indicating the isotropic characteristics of the ECA. The ECA sample with a smooth frictionless surface. As shown in Fig. 7, most of the Ag nanopowders fuse together to form a network throughout the entire film.

The chemical structures of the silver nanopowders and cured ECA composite with 75% silver nanopowders were researched by FTIR spectra (Fig. 8). Fig. 8 shows the strong absorption peak of pure silver nanopowders at 3427cm^{-1}, 2347cm^{-1}, 1639cm^{-1} and 1384 cm^{-1}. As described in Fig. 8b, ECA composite film shows weak absorption peak in the spectrum. These absorption peaks decrease with the addition of silver nanopowders. The FTIR spectroscopy measurement indicates that silver nanopowders have been grafted into epoxy resin matrix.

4 Conclusion

In this work, spherical silver nanopowders were produced by DC arc plasma method with smooth surface. The silver nanopowders present a diameter range from 15 to 220 nm. The ECA was prepared using silver

nanopowders as conductive fillers, and could be shaped by screen printing method. The ECA can be printed on PET and metal substrates and be cured in the air at 150℃ for 10 min. The ECA with the 75% silver nanopowders shows an excellent electrical conductivity and bonding strength. The percolation region for this ECA fall in the region of silver filler with 75% and the resistivity of ECA reached $9.5\times10^{-4}\Omega\cdot cm$. The ECA has high strength, and it has potential applications in flexible printed electrodes and interconnecting materials.

Declarations

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Declaration of Interest Statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Preparation of silver nanopowders and its application in low temperature electrically conductive adhesive”.

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Figures

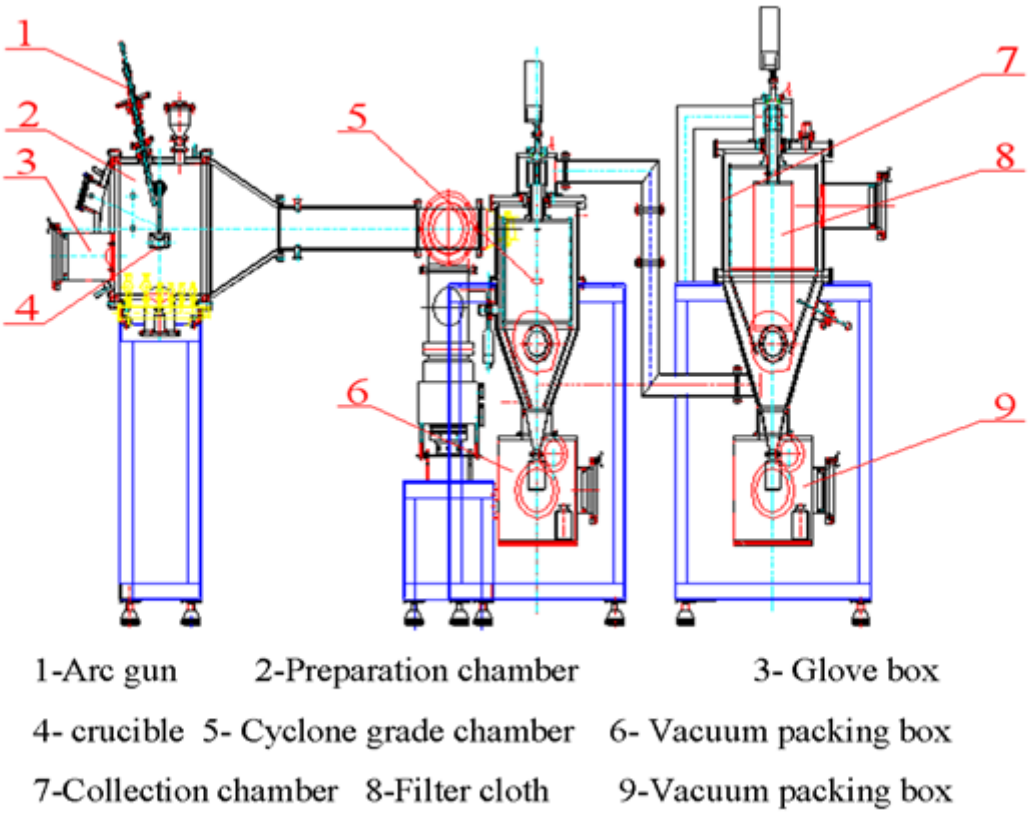

Figure 1

The diagram of direct current arc plasma evaporation device

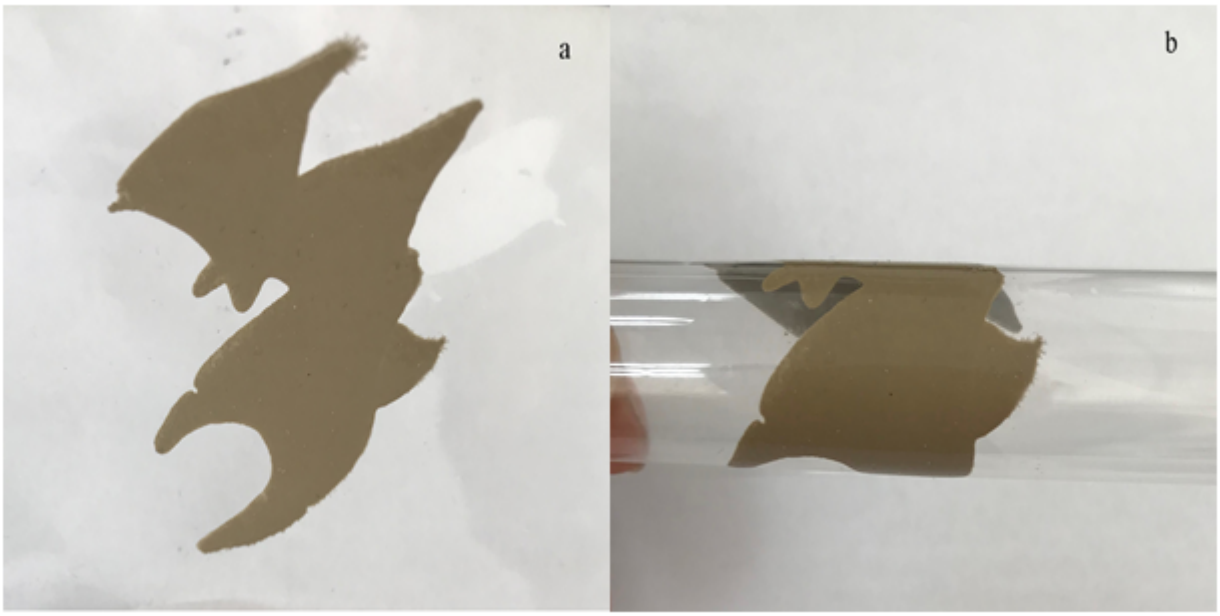

Figure 2

Demonstrations of the printability of the Ag ECA. ((a) and (b) screen printed mages of school badge under different deformations)

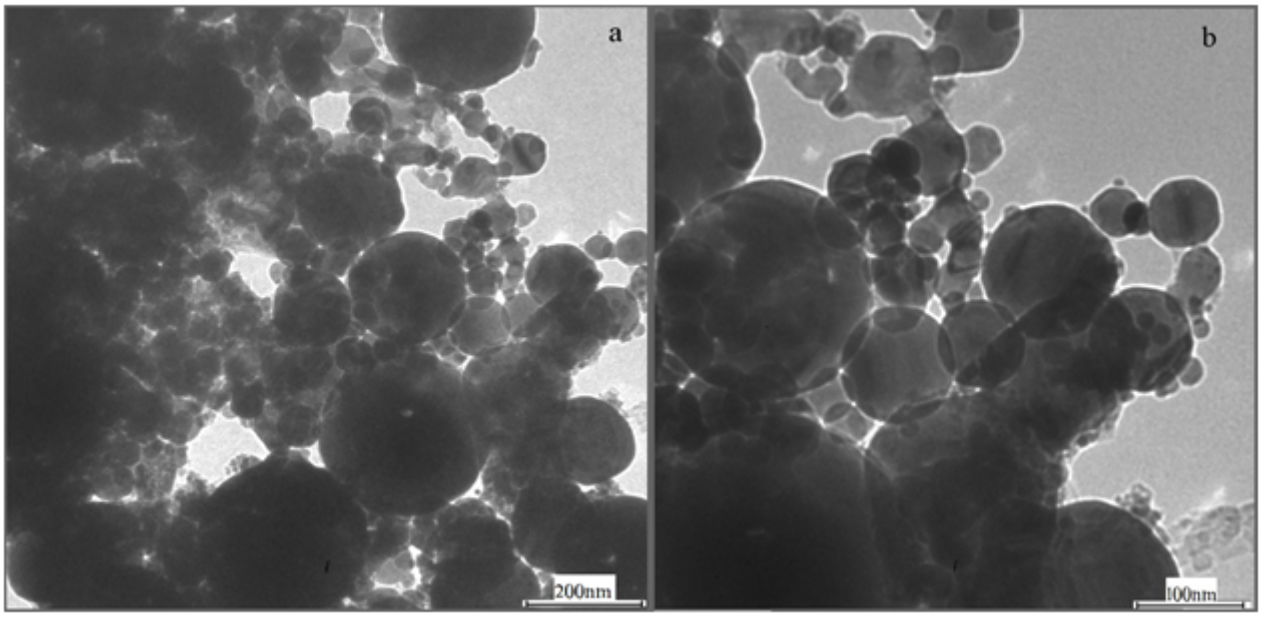

Figure 3

TEM images of silver nanopowders ((a) low magnification and (b) high magnification).

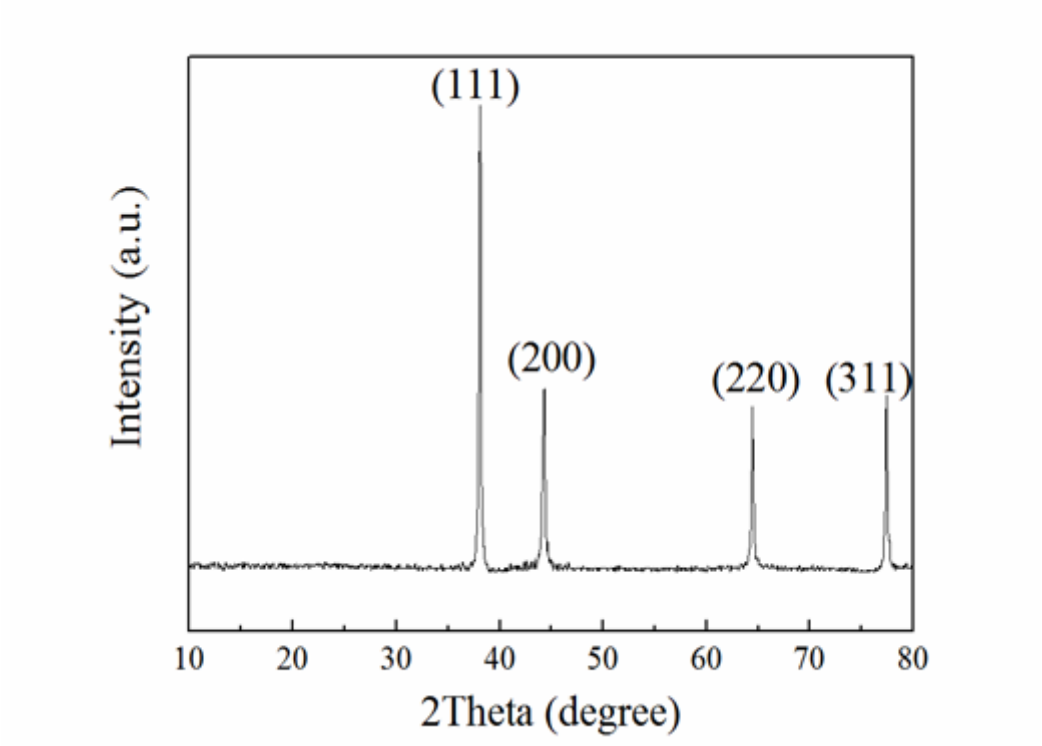

Figure 4

XRD pattern of the silver nanopowders

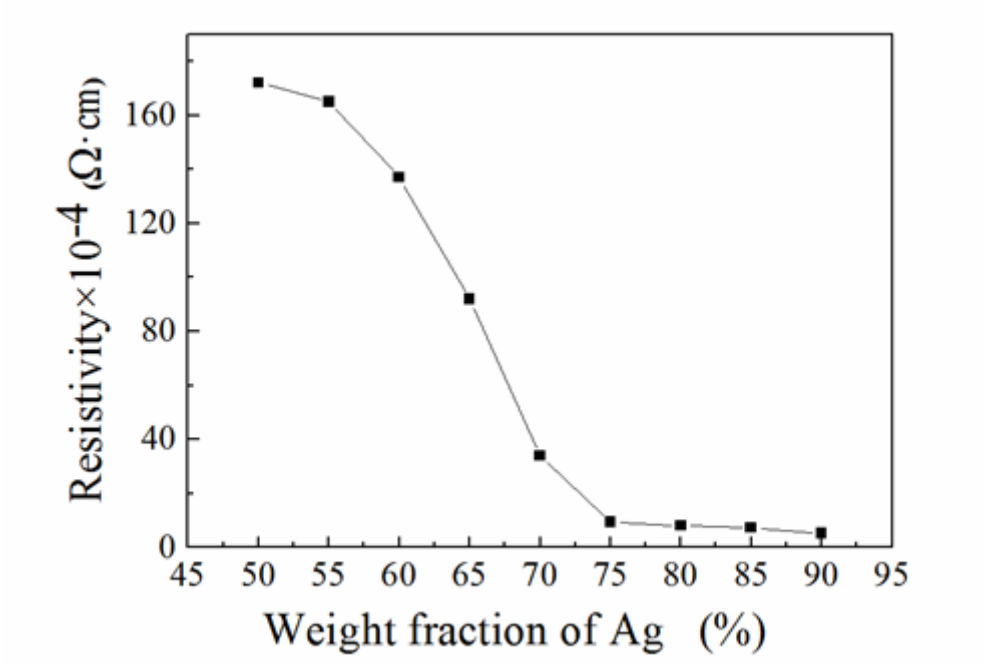

Figure 5

Electrical resistivity of the cured ECA as a function of Ag weight fraction

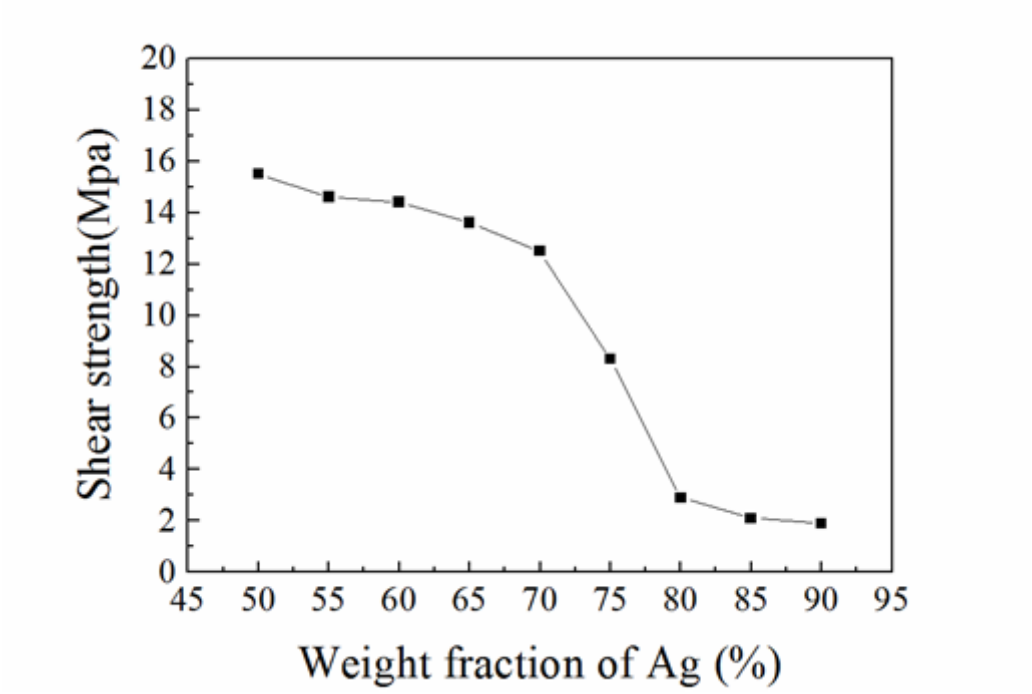

Figure 6

Shear strength of the as cured ECA as a function of Ag weight fraction

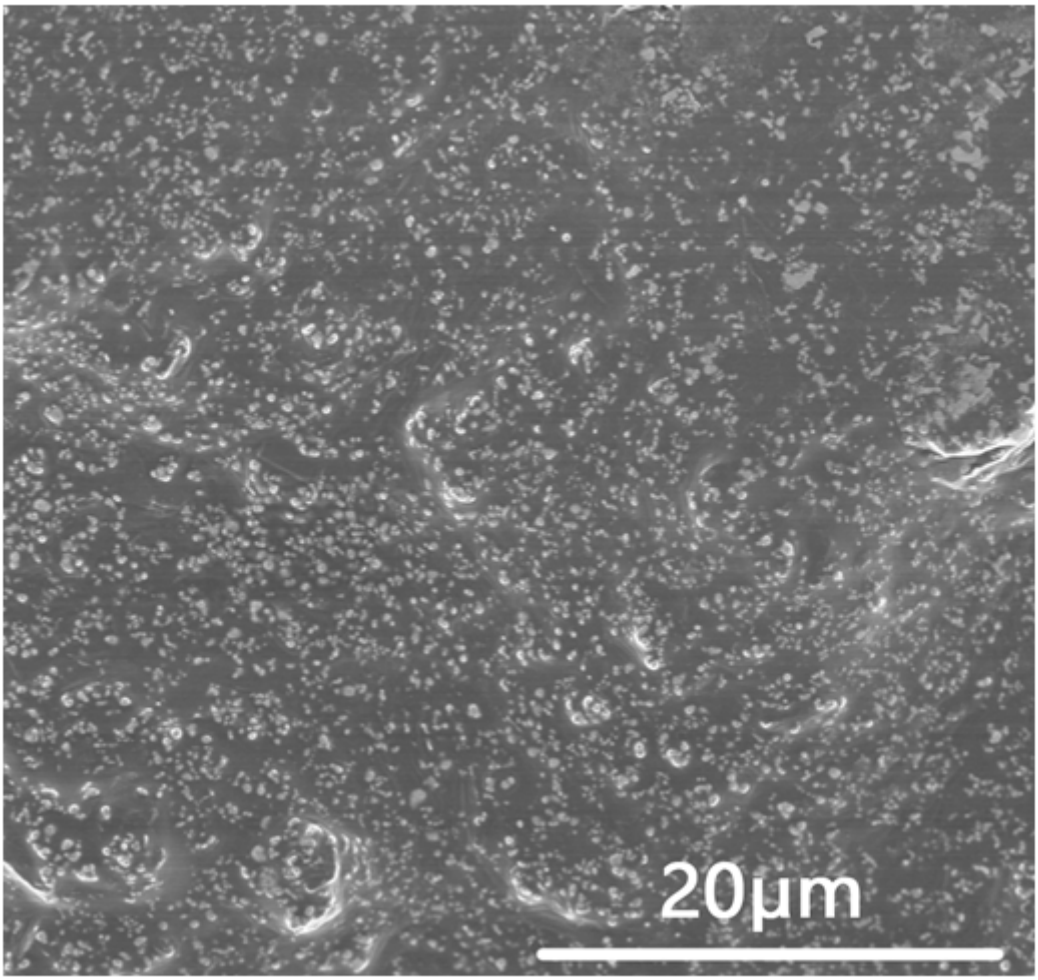

Figure 7

SEM images of the cured ECA conductive polymer film filled with 75% silver nanopowders

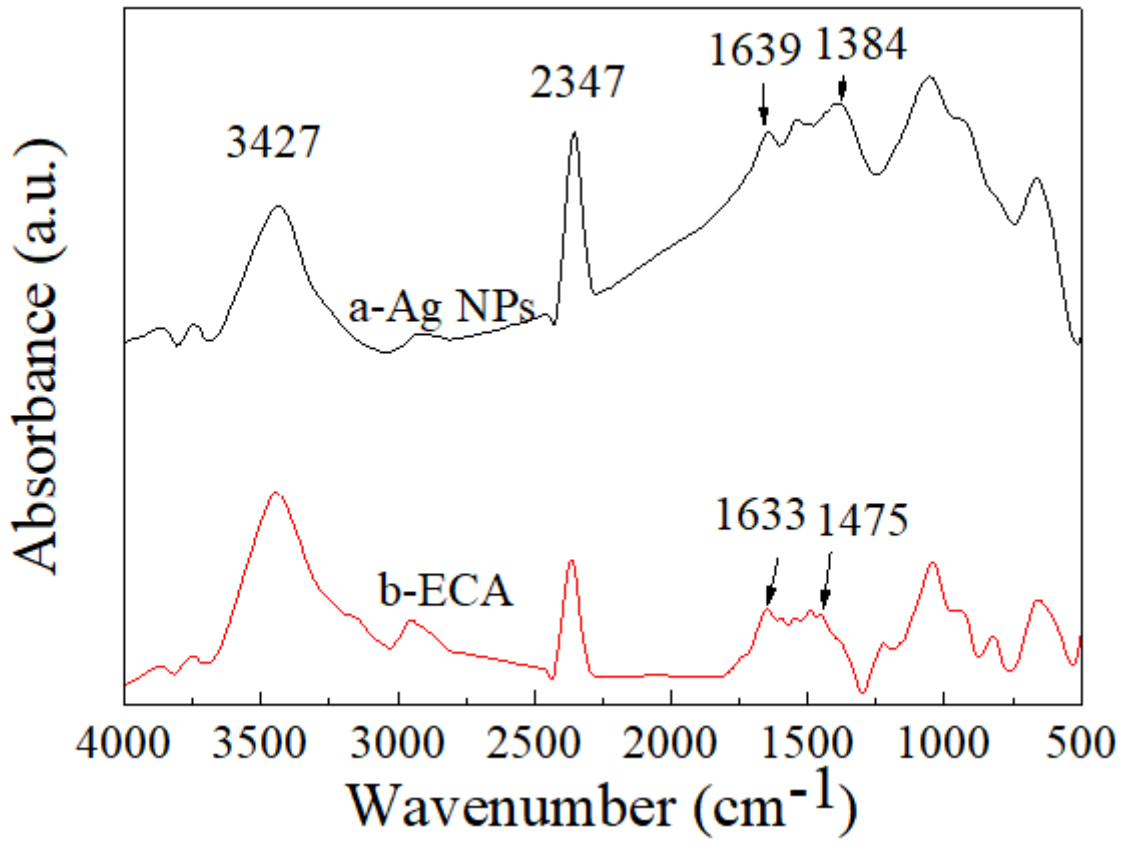

Figure 8

FTIR spectroscopy of the silver nanopowders and cured ECA conductive polymer film filled with 75% silver nanopowders