Anisotropic Conductive Film (ACF) Prepared from Epoxy/Rubber Resins and Its Fabrication and Reliability for LCD

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Abstract

A thermoset type anisotropic conductive adhesive film (ACAF) comprising epoxy resin and natural butyl rubber (NBR) as the binder, micro-encapsulated imidazole as the curing agent, and Ni/Au coated polymer bead as a conductive particle has been studied. These films have been prepared to respond to requirements such as improved contact resistance, current status less of than 60 μm and reliability. These films can also be used for connection between the ITO glass for LCD panel and the flexible circuit board. The curing conditions for the connection were 40, 20 and 15 seconds at 150, 170 and 190 ℃, respectively. The initial contact resistance and adhesion strength were 0.5 Ω/square and 0.4 kg/cm under the condition of 30 kgf/㎠, respectively. After completing one thousand thermal shock cycling tests between –15 ℃ and 100 ℃, the contact resistance was maintained below 0.7 Ω/square. Durability against high temperature (80℃) and high humidity (85 % RH) was also tested to confirm long-term stability (1000 hrs) of the conduction.

Keywords : anisotropic conductive (adhesive) film; ACF, electrical conduction, LCD Packaging, reliability.

1. Introduction

Recently, liquid crystal display (LCD) panels have become very important components in mobile electronics. An LCD module is made up of an LCD panel device, source and gate drivers, gate array, printed-circuit boards (PCBs), interface circuits, a back-light, connectors, and frame and covers, etc. The quality and reliability of the LCD module depend on the way in which the driver integrated circuit (IC) is attached to the panel. As a high-density interconnector material, anisotropic conductive adhesive film (ACAF or ACF) is the most popular material for attaching the tape-carrier packages (TCPs) and the tape automated bonding (TAB) and chip-on-glass (COG) packages of the driver IC to the LCD panel. In recent years, ACF have also been utilized as the flip-chip [1,2] and flip-chip-on-glass (FCOG) [3] interconnections.

ACF, which is generally referred to as "z-direction conductive adhesive materials" is composed of an adhesive thermoset polymer matrix and fine conductive fillers such as metallic (Ni) particles [4] or metal (Ni/Au)-coated polymer balls [5,6] while the electrical isolation in the x-y direction is maintained. Electrical conduction is generated through the conductive fillers trapped between the mating input/output(I/O) pads when the heat and pressure are applied. For the adhesive polymer matrix, the mixed resin of thermoplastic elastomer and thermosetting epoxy polymer is used to provide electrical insulation, to protect the metallic contacts from mechanical damage, and to provide stable adhesion. Thermoplastic resin adhesive is easy to repair, but unfortunately has poor stability at high temperatures. The adhesion is not strong enough to hold the conductive particles in position, and the contact resistance fend to increases after thermal shocks. To overcome these disadvantages several thermosetting epoxy resins have been developed [4,7,8]. In general, the thermosetting epoxy adhesive materials are known to be very stable at high temperature and, more importantly, gives low contact resistance. This type of ACF is in use in various

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applications. However, with the advancement of LCD technology, ACF can now to respond to requirements such as improved contact resistance and pitch interval (corresponding to finer circuit pattern) from device makers, and reliability. Normally, in order to attach the driver IC TCPs to the glass panel, for 10-12 inch SVGA/XGA, about 280-320 electrodes per TCP with 60-80 μm pitch are required for a productive connection process. ACF provides for the following good properties for LCD applications: 1) numerous electrodes with micro-pitch (10-15 electrodes per mm) can be connected simultaneously; 2) acceptable bonding conditions (below 170 ℃/20 seconds) are provided for TCPs and LCD glass panels; and 3) mechanical and electrical contact and reliability of contact required for the LCD application are achieved. More recently, ACF bonding conditions at lower temperature are also required.

In this study, we report a thermoset type ACF prepared from epoxy/rubber resins and its fabrication and reliability for LCD. We will discuss the effects of bonding temperature, time and particle properties on contact resistance, adhesion strength, and reliability of ACF interconnection.

2. Experimental

The epoxy resin of bisphenol A type, natural butyl rubber (NBR) and silane-coupling agent were dissolved in toluene at 60 ℃ for over 5 hrs. The solution was then cooled to room temperature and a micro-encapsulated imidazole (Asahi Chemical Ind., Novacure® HX3748) as the curing agent was added. Then, Au/Ni coated polystyrene beads (Sekisui fine chemical co.) cross-linked with divinyl-benzene [5,6] were added to produce a final 45 wt% adhesive solution. Our formulation is shown in Table 1. The particles were 5 and 10 μm in diameter. The thermoset resin of the mixture of epoxy and NBR was used as the insulating resin due to its strong adhesion to various substrates (ITO glass, flexible printed circuit (FPC) and TAB, etc.) and favorable melt viscosity. The solution was coated using a comma direct coating method onto a silicone-treated polyethylene terephthalate (PET) film which was 50 μm in thickness (release film RR CF503 provided by Saehan), the adhesive layer (ACF layer) at dry state after coating was about 25 μm in thickness. In this case, the PET film acts as a liner or separator for the resulting ACF.

Table 1.

Materials		Weight(%)	Remarks
Epoxy resin	Bisphenol a type of high EQ	17	Epoxy equivalent 2000 g/mol
	Bisphenol a type of low EQ	17	Epoxy equivalent 450-500 g/mol
NBR	Natural butyl rubber	17	N34, Nippon Zeon
Curing Agent	Microcapsulated imidazole	43	HX 3748& HX 3722, Asahi chemical
Coupling Agent	Epoxysilane coupling agent	0.5	A-187, Nipon Unicar
Conduction Filler	Au/Ni coated polystyrene bead	5.5	Au 210, Sekisui Fine Chemical

A Perkin-Elmer DSC-7 was used to measure the glass transition temperature (T_g) of the epoxy/rubber thermoset resin. The dynamic scanning temperature ranged from −10 to 250 ℃. The isothermal curing reaction was also investigated at three isothermal curing temperatures of 150, 170, and 190 ℃. Measurements were taken on 10mg samples at a heating rate of 10 ℃/min. The Instron model 4202 was used to measure the adhesion strength. A JEOL J840 scanning electron microscope (SEM) was used to investigate the dispersion and the morphologies of the conductive filler (particles) before and after bonding. For the evaluation of the ACF interconnection, contact resistance and adhesion strength between FPC and ITO glass were measured. The contact resistance was measured by a typical four-point probe method using 1 mA current. The peel strength test was carried out at an angle of 90 °.

The adherence of ACF interconnection was a blank ITO deposited glass with sheet resistance of 8-10 Ω/sq. and FPC with patterned, metallized input/output (I/O) pads. The metal pad on flexible film (FPC) consisted of approximately 35 μm thick copper, electrically plated 0.5-2 μm gold on the top. The pad length was 2.5 mm and the pad pitch 180 μm. Our heating and pressurization (bonding) equipment is shown in Fig. 1.

ACF was first attached to the surface of the electrodes of the glass panel or FPC (or TCP) at 60-70 ℃ for 1 to 3 seconds. At the next step, the FPC electrodes were aligned with the electrodes on the glass panel and pre-bonded under the conditions described above so that an accurate alignment can be achieved under the temperature of 80 ℃ and 5-6 kgf/㎠. Finally, the ACF was completely cured when heated at 150-190 ℃ for 15-40 seconds. In general, an adhesive temperature was set to 170 ℃, and allowed bonding to proceed for about 20 seconds for most of the experiments. Before bonding, all pieces of ITO glass panel and FPC were carefully washed using organic solvents in order to remove any organic contaminants that might have an adverse effect on ACF interconnection. The bonding pressure was applied under the conditions of 10, 20, and 30 kgf/㎠.

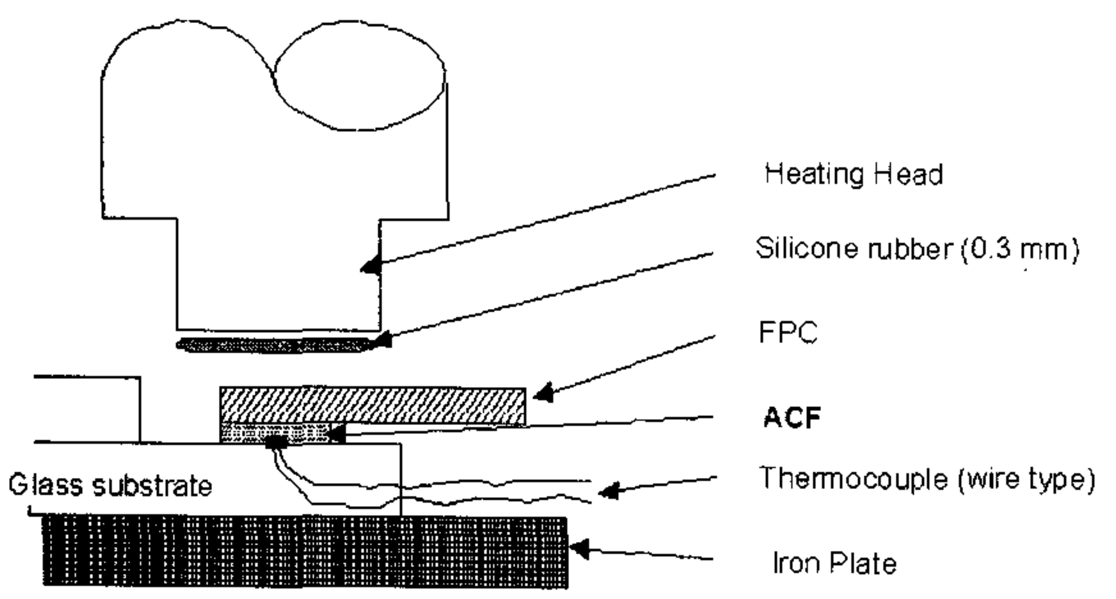

Fig. 1. Apparatus used for heat-seal pressing of ACF.

Reliability evaluation of the samples produced was accomplished using two types of environmental test such as aging test under high temperature/high humidity and thermal shock test (temperature cycling test). Adhesion strength measurements were taken only on a before- and after-test basis. Measurements of the surface insulation resistance and contact resistance under temperature cycling conditions were taken continuously without removing the samples from the test chamber. The aging test was performed using an Espec Temp. & Humid SH-240 chamber. Test was conducted at a temperature of 80 ℃ and the relative humidity was maintained at 85 %. The test was conducted for 1000 hrs. To measure the change of electrical performance throughout the test, the samples were removed from the chamber for connect resistance measurements after 250, 500, 750, and 1000 hrs. The thermal shock test was also performed using an Espec Temp. & Humid SH-240 chamber, and the specimens were subjected to one thousand heating and cooling cycles from temperatures of -15 ℃ to 100 ℃. The holding time at each temperature extreme was 60 min and the transition time was 45 min. The heating and cooling rate for these cycles was approximately 0.4 ℃/min. Measurements (the connection resistance and the adhesion strength) after 200, 400, 600, 800, and 1000 cycles were taken at room temperature.

3. Results and Discussion

ACF and its unique properties have been accepted because of the requirements of LCD applications, such as electrical contact resistance and usage temperature. The bonding condition, in particular, temperature range for LCD packaging, during the ACF connection can be determined from the DSC dynamic scan. The selection of curing agent with thermoset resin was done considering the long shelf life and fast-cure properties. The prescribed amount of curing agent was added to each 100 g of bisphenol A type epoxy, and gel time was measured at 150, 170, and 190 ℃. Micro-capsulated 2-methylimidazole showed the best performance. The curing agent, 2-methylimidazole was adducted with the bisphenol A type epoxy, first, and modified with isocyanate to give a urethane shell. The problem with this curing agent is the susceptibility of the microcapsule to polar solvents, such as alcohols or ketones. For this reason, we selected a toluene as the solvent because it is good for protecting microcapsule. Another reason for adding to the mixture a silane coupling agent was to improve the durability of conduction. In general, the silane coupling agents improve durability; we selected γ-glycidoxypropyl trimethoxysilane, that showed the best performance. Our

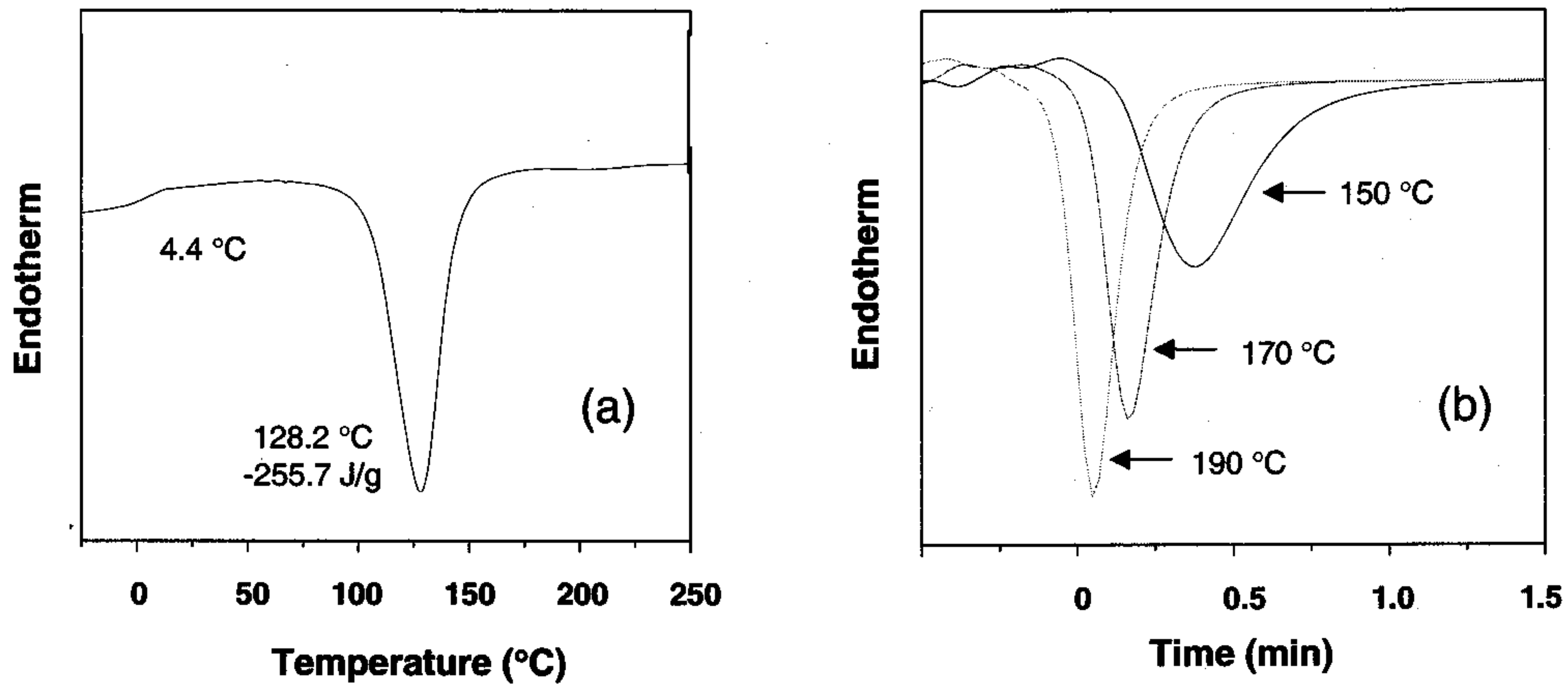

Fig. 2. Thermal curing conditions by DSC: (a) curing of ACF in the dynamic mode at 10 ℃/min heating rate; and (b) isothermal DSC thermogram at 150, 170, and 190 ℃ scan.

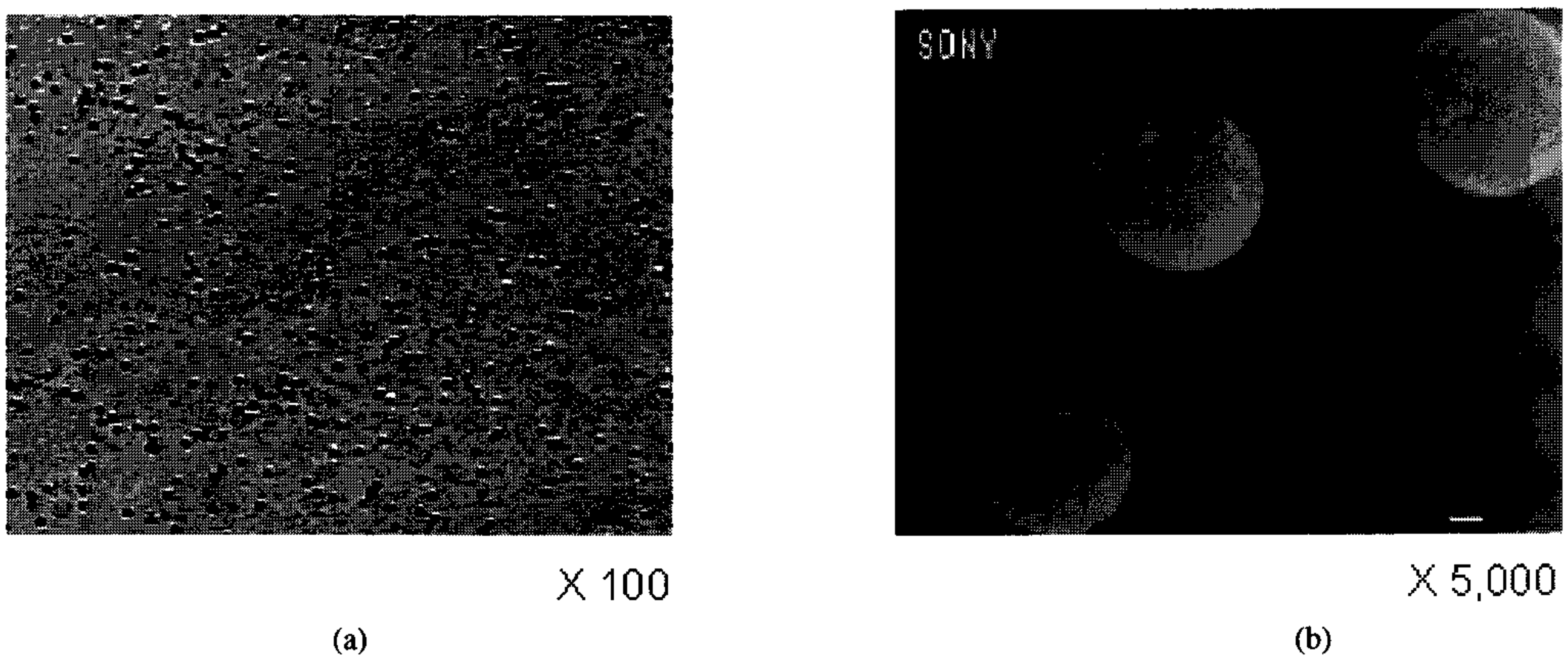

Fig. 3. Dispersions of conductive particles in ACF measured using (a) optical-microscope and (b) SEM.

formulation (Table 1) shows a flexible and thermal pressure sensitive ACF having fast-cure and long shelf-life properties.

DSC was used to study the thermodynamics of epoxy/rubber blended ACF in the formulation as shown in Table 1. Fig. 2-a. shows a typical DSC melting endotherm obtained for the blend samples. The diagram shows glass transition temperature (T_g) of the blended polymer at 4.4 ℃, melting endotherm at 128.2 ℃, and heat of fusion of 255.7 J/g. Isothermal DSC thermograms were also used for epoxy-curing studies. Fig. 2-b shows a typical isothermal DSC thermograms normalized with sample weight at the curing temperatures of 150, 170, and 190 ℃. The endotherm at 190 ℃ is sharper compared to those at 150 and 170 ℃, indicating faster reaction. From the DSC dynamic scan, the stable bonding conditions seem to be deduced by measuring the extent of the epoxide cure reaction or by accurate measurement of time interval between a discernible beginning and the end of a cure reaction. The stable bonding conditions from this analysis were found to allow bonding to proceed for 40, 20, and 15 seconds at 150, 170, and 190 ℃ respectively. The fast cure with the long shelf life is a very important property of ACF.

Appropriate amount, of Ni/Au coated polystyrene beads were added to the adhesive film as a conductive particle to meet pitch interval less than 60 μm corresponding to finer circuit pattern. Fig. 3 shows a representative optical (x 100) and electron (x 5000) micrographs of conductive particles after ACF manufacturing. The contact resistance of ACF was further improved by Ni balls with Au-coated Ni balls,

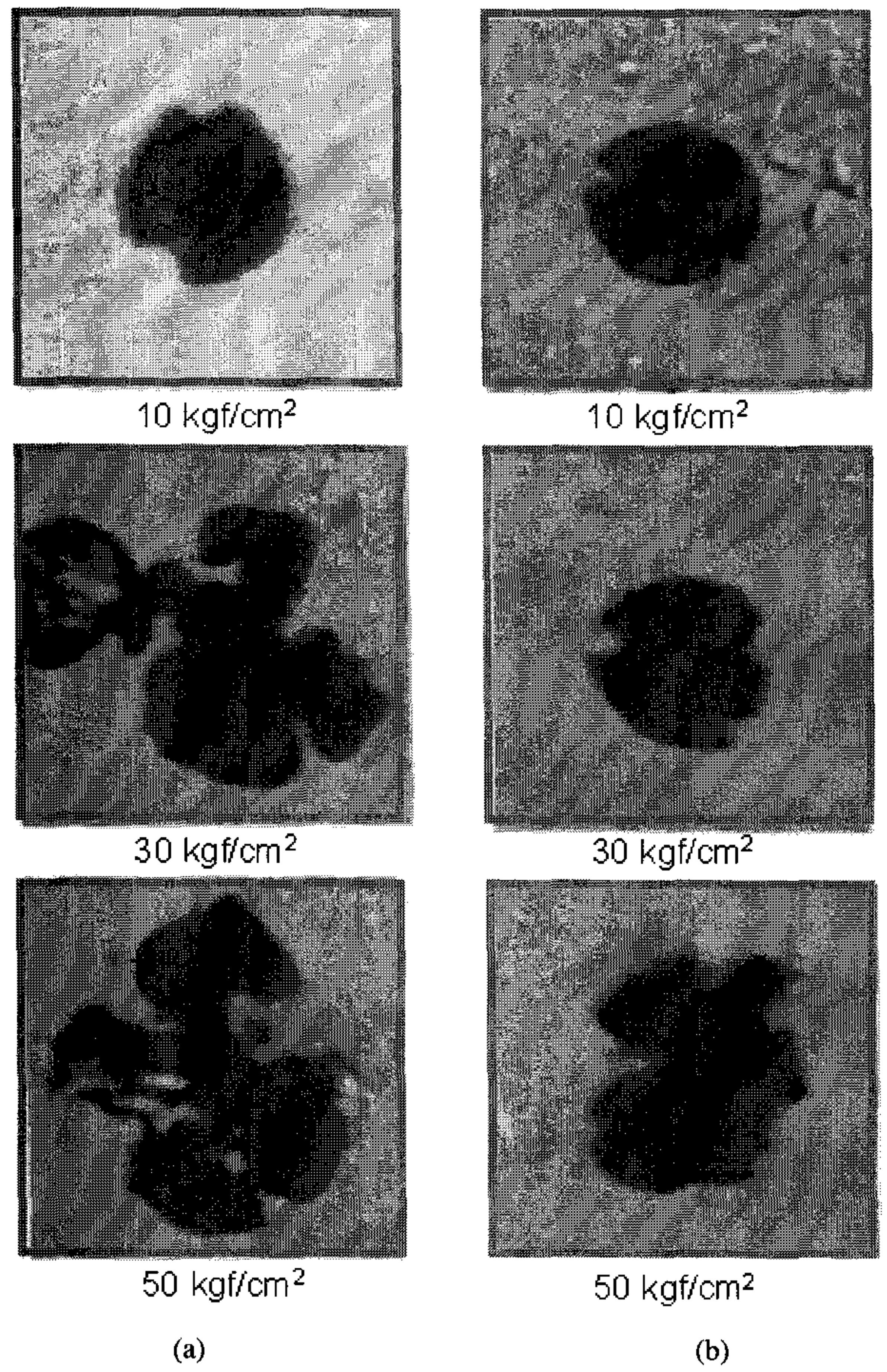

Fig. 4. The optical micrographs of conductive particle in ACF after applying pressure of 10, 30, and 50 kgf/㎠: (a) 10 μm and (b) 5 μm particles.

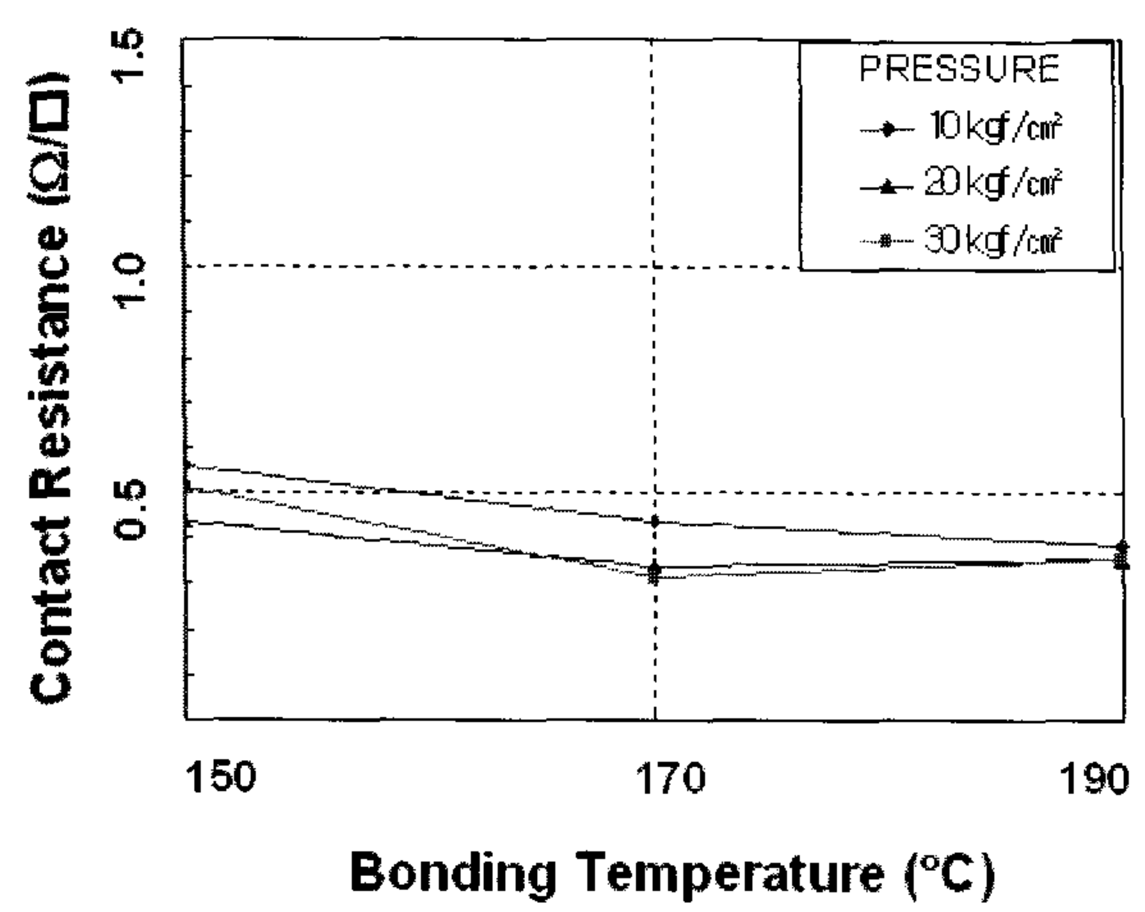

Fig. 5. Contact resistance as a function of bonding temperature and pressure.

which have been replaced with Ni/Au coated polystyrene (PS) beads crosslinked with divinyl benzene [5,6]. These tiny metal coated PS beads deform when heated and pressed above 100 ℃ to give wider contact area between electro terminals. A further trial has been made to obtain fine pitch connection in which the metal-coated PS beads are again coated with an insulating resin; the insulating resin is broken only under pressure to expose the conducting layer on the PS sphere. Because the thermal expansion coefficient of metal-coated PS beads is very close to that of thermoset adhesive, the combination of epoxy resin and metal-coated PS beads greatly improves thermal stability. Fig. 4 shows the optical micrograph of conductive particle in ACAF after applying pressure of 10, 30, and 50 kgf/㎠ gradual increase in pressure we could observe particles rupturing. The particle appears to break when internal stress exceeds a certain threshold value. Breakup of particle was observed at 30 kgf/㎠ and at 50 kgf/㎠ for particles with 10 μm and 5 μm diameter, respectively. Based on these observations, pressurization for ACF connection was done under the conditions of 10, 20, and 30 kgf/㎠

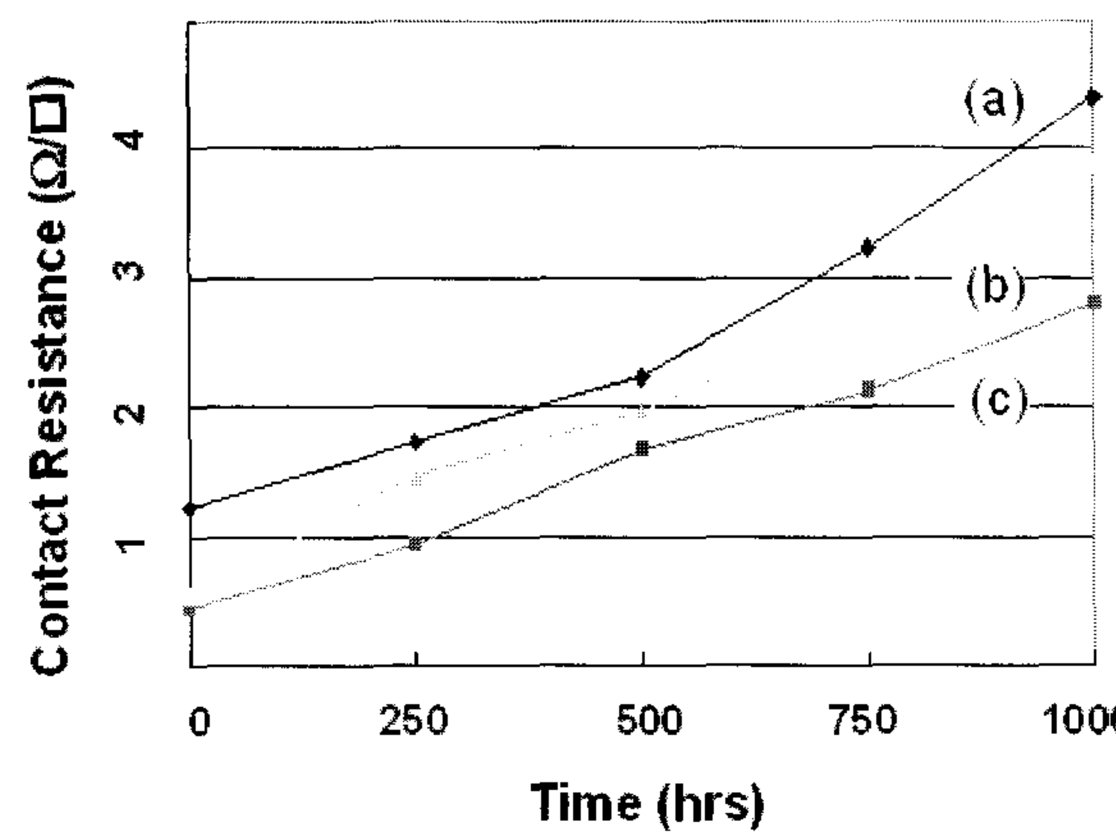

Fig. 6. The changes of contact resistance after aging test for 1000 hrs at the temperature of 80 ℃ and 85 %RH: bonding conditions are (a) 150/40, (b) 170/20, and (c) 190 ℃/15 seconds, and pressure was maintained at 30 kgf/㎠.

Figs. 5, 6, 7 and 8 show the bonding reliabilities of ACF after connection. Fig. 5 shows the initial contact resistance when ACF is connected at temperatures of 10, 20, and 30 kgf/㎠. All samples prepared at temperatures of 150, 170, and 190 ℃ indicate contact resistance of below 0.6 Ω/square. The contact resistance was found to decrease with increasing bonding temperature or pressure. Especially, the decrease in contact resistance with increasing bonding force was due to the improved flowability of ACF thermosetting binder, which helps to make better contact between the electrode and conductive particles. Paik et al. [9] have reported the high contact resistance at the bonding pressure of above 30 kgf/㎠. It is carried out proposed that such high contact resistance is due to the bouncing effect of the epoxy resin after the pressure release. Figs. 6 and 7 show the changes of contact resistance and adhesion strength (peel strength) after aging test was carried out for 1000 hrs at a temperature of 80 ℃ and 85 %RH (bonding tempera-ture were varied with 150/40, 170/20, and 190 ℃/15 seconds, while pressure is fixed at 30 kgf/㎠). The contact resistance and adhesion strength after aging test was conducted for 1000 hrs increased as the aging time increased. As bonding temperature or aging time increased, the degree of cure of epoxy-based adhesive also increased, which resulted in stronger chemical bonding at the interface and excellent adherence. During the aging test, under the conditions of the 80 ℃/85 %RH, the humidity causes hygroscopic expansion of epoxy and weakening of adhesion between epoxy and contact pad , resulting in a contact resistance increase.

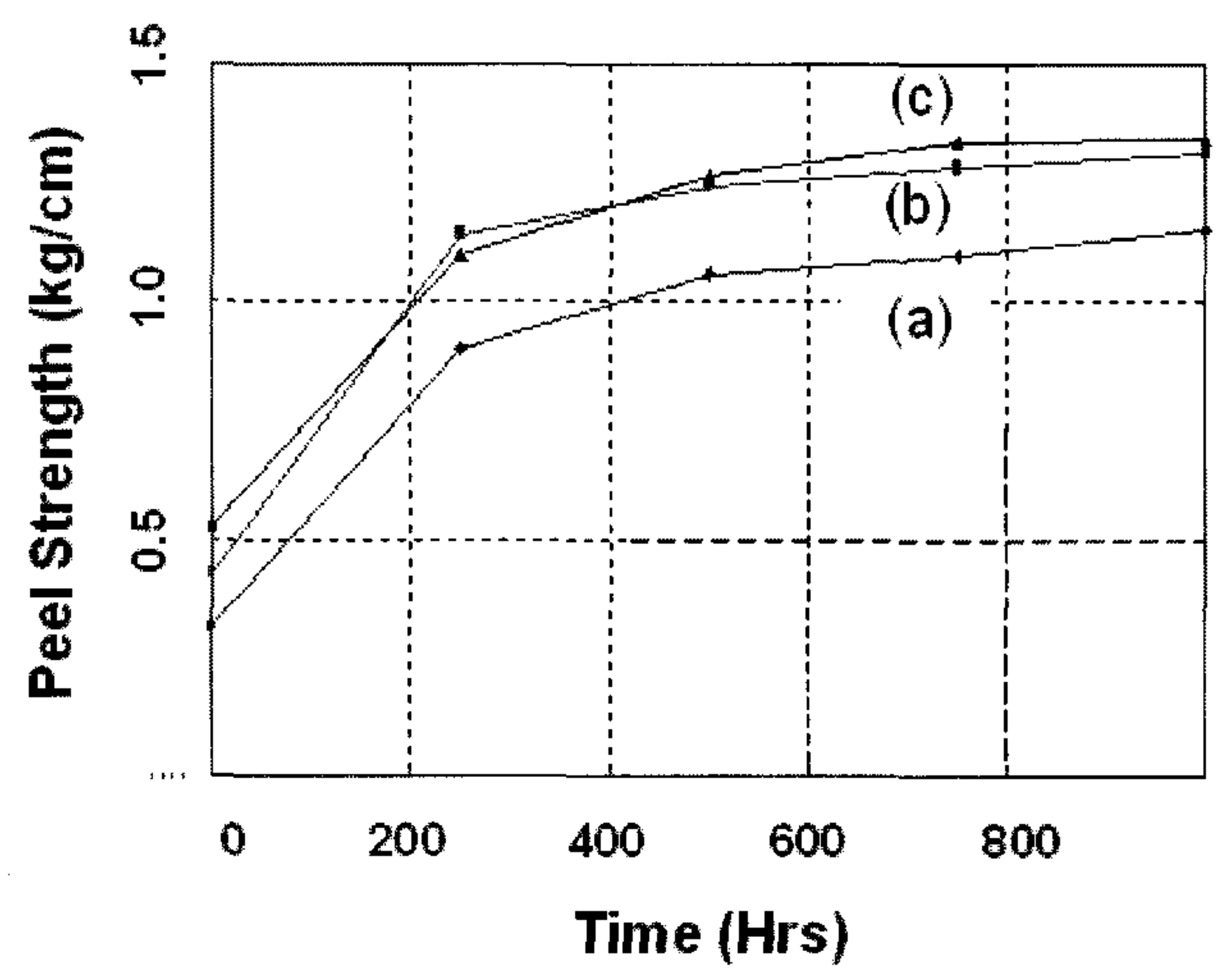

Fig. 7. The changes of adhesion strength (peel strength) after carrying out aging test for 1000 hrs under the conditions of 80 ℃ and 85 %RH: bonding conditions were (a) 150/40, (b) 170/20, and (c) 190 ℃/15 seconds, and pressure was fixed at 30 kgf/㎠.

Based on observation using electron probe microanalysis on a cross-sectioned joint of catastrophic bonding failure after a temperature/humidity test [11] the oxidation of the metallic ball was also attributed to the increased contact resistance [10]. Fig. 8 shows the changes of contact resistance under thermal shock test between -15 ℃ and 100 ℃ for 1000 cycles (bonding temp. and pressure were fixed at 170 ℃/20 seconds and at 30 kgf/㎠/20 seconds). The contact resistance did not produce any significant change under thermal shock. However, the contact resistance did show a small increase with the increasing number of cycles.

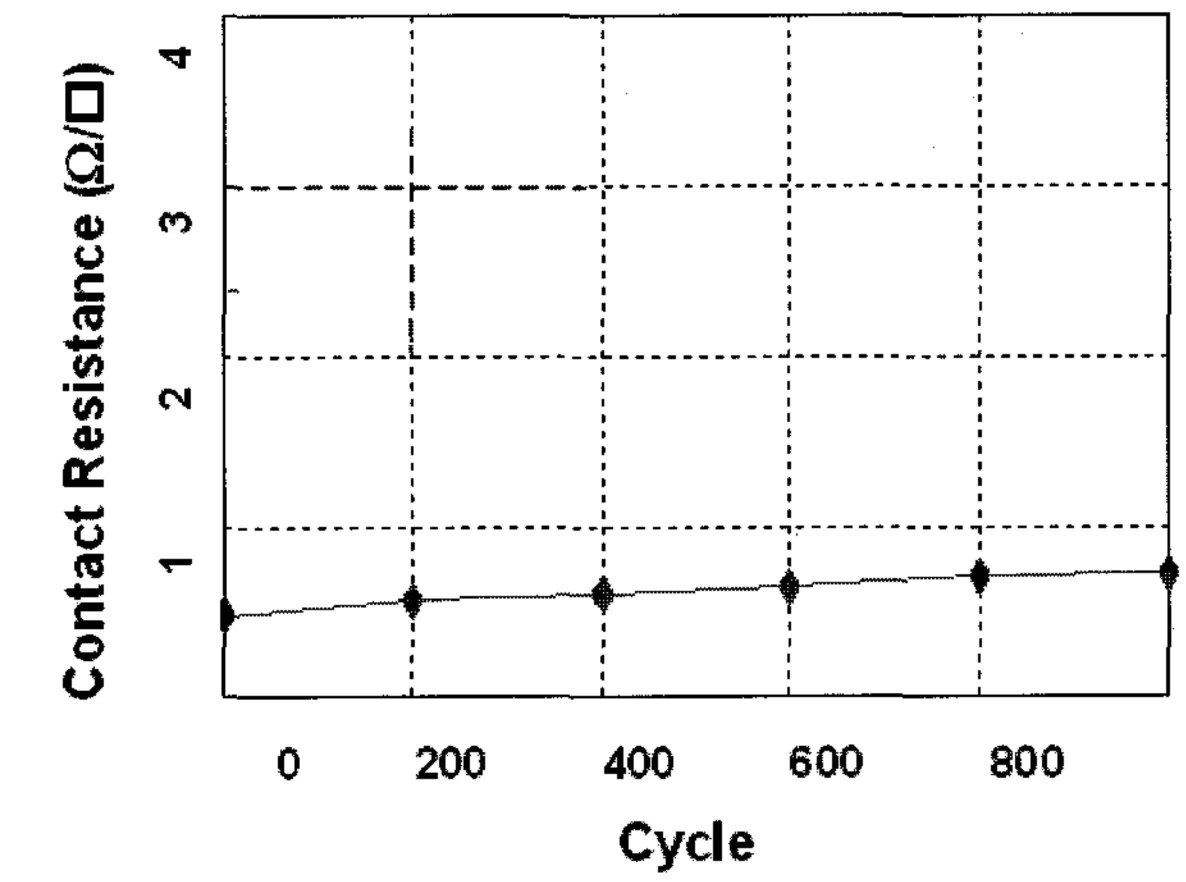

Fig. 8. The changes of contact resistance under thermal shock test between -15 ℃ and 100 ℃ for 1000 cycles.

4. Conclusion

A thermoset type ACF has been developed to respond to the requirements such as improved contact resistance, current status to less than 60 μm, and reliability. A thermosetting epoxy resin coupled with natural butyl rubber (NBR), and micro-encapsulated imidazole was used as a matrix resin and Ni/Au coated polymer bead as a conductive particle for ACF. After cure, various good electrical and mechanical properties were obtained. The durability tests at temperature ranging from 80 ℃ to 85 %RH and the thermal shock test between -15 ℃ and 100 ℃ showed excellent performance. The strength in the adhesion after curing was enough to sustain good conduction between an ITO glass and Cu-patterned polyimide film (FPC). Lastly, the gel time (170 ℃) and the contact resistance (0.5-1.0 Ω/square) of the film were as low as those of the commercially available ACF samples.

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