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A study of adhesive improvement of a Cr-Ni alloy layer on a liquid crystal polymer (LCP) surface

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ABSTRACT

To improve adhesion of an alloy plating layer made from chromium (Cr) and nickel (Ni), surface modification effects produced by low pressure nitrogen (N_2), oxygen (O_2), or argon (Ar) gas plasmas on a liquid crystal polymer (LCP) film were analyzed with X-ray photoelectron spectroscopy (XPS). Furthermore, we focused on motion of the LCP main chains caused by macro-Brownian motion and found that reducing the glass-transition temperature of liquid crystalline by annealing further improves adhesion between the alloy plating layer and LCP.

1. Introduction

In recent years, there is an increasing demand for liquid crystal polymers (LCPs), especially for precision parts used in the electric, electronic, and information communication fields [1]. What lie behind this is their high heat resistance that enables them to withstand lead-free solder, low water absorbency that leads to little in the way of dimensional changes caused by humidity, low gas emission that protects metal contacts from corrosion, and excellent injection moldability that is suitable for the abovementioned uses as requirements become denser and finer. Additional factors responsible for the increased demand is that LCPs are basically recyclable and exhibit flame retardancy without the addition of any flame retardants, that is, LCPs meet the needs of this age of environmental awareness.

The type of used LCPs is roughly classified into three fields: injection molding, fibers, and films. In the field of film, in particular, development of applications focusing on LCPs' excellent electrical properties and heat resistance continues to be actively promoted. One of these applications is using as an insulating film for flexible printed circuits (FPCs). Commercialization for FPCs has already begun by making full use of LCPs' thinness, flexibility, and properties that are comparable to expensive ceramic materials, such as heat resistance, low water absorbency, and low dielectric loss at a high frequency [2–5].

In flexible copper clad laminated sheet (FCCL) for FPC, polyimide (PI) is used as an insulating material and on the PI a seed layer and copper (Cu) are deposited. Such a FCCL for FPCs is used as chip on film (COF) packaging in electrical devices including a liquid crystal display. Although PI film has been used as a standard substrate for FPC due to its excellent mechanical strength and electrical properties, PI film has a disadvantage in high moisture absorbency, resulting in problems with dimensional accuracy and electrical properties in a highly humid environment [6]. Against this backdrop, a new double-sided FCCL consisting of LCP film as an insulating material and Cu is being developed. However, poor adhesive strength between the LCP film and Cu has become a problem [7]. Various methods have been developed to improve the poor adhesive strength and surface modification by plasma is the most effective treatment method to introduce polar groups into the surface of LCP film [5,8,9].

Because a LCP forms polymer domains and specifically exhibits liquid crystal phases, as shown in Fig. 1, there is a problem of low adhesion with dissimilar materials due to the marked orientation of polymer chains toward the flow direction, delamination by application of a strong external force, and the cohesive forces among the liquid crystal molecules themselves [10]. These characteristics originate from the rigidity and inflexibility of the molecular chains

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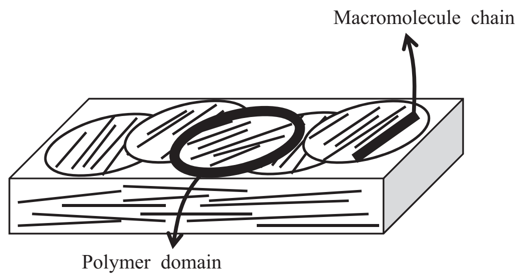

Fig. 1. Molecular orientation in a LCP film.

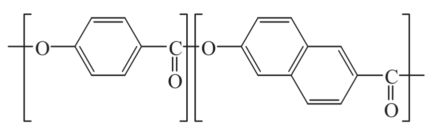

Fig. 2. Chemical structure of Vecstar LCP film material.

of LCPs. On the other hand, noncrystalline polymers such as epoxy resins and urethanes are flexible and are entangled with each other and therefore such a problem seldom arises.

To improve the adhesion, roughening of the metal layer and film surface (e.g. by sandblasting and chemical treatment) to increase the adhesion surface area and surface treatment of the film (e.g. corona discharge, ultraviolet irradiation, excimer laser irradiation, and plasma treatment) have been proposed also for LCP [11,12]. However, because electrical signals flow across the interface between the metal layer and the insulating material due to the skin effect in high-frequency bands and the highest possible smooth adhesive interface is favorable for transmission, excessive roughening treatments are not suitable.

Under these circumstances, plasma irradiation treatment is expected to be a method that can modify the LCP surface while keeping the surface smooth. Because electrons and ions in a plasma have large amount of electrical energy, the polymer surface irradiated by the plasma is etched and contaminants on and in a weak boundary layer of the LCP film are removed. In addition, radicals in the plasma are highly reactive and therefore react chemically with the polymer surface, resulting in the introduction of functional groups into the polymer surface and increase in affinity to metals [8].

In this paper, the adhesion mechanism between LCP and the metal layer, which is especially important, was investigated and, on the basis of the results, conditions of surface modification that can improve adhesion of LCP film and measures for their improvement were examined and proposed.

2. Experimental

2.1. Preparation of metalized film

Fig. 2 shows the chemical structure of a LCP film of 50 μm thickness (Vecstar, Kuraray) that was used for the substrate. Vecstar is made from polyarylate liquid crystalline polymer as a raw material and consists of a chain of *p*-hydroxyl benzoic acid and bioxide-6-naptholine acids. This LCP film is a high-performance polymer having a high glass transition temperature, low dielectric constant, and low thermal expansion coefficient.

The LCP film was modified by plasma in a vacuum (at 3 Pa, 25 °C), where the N_2, O_2 or Ar gas was introduced at fixed flow rate of 3.0×10^{-2} m^3/h and with the power of 1.1 kW. Subsequently, a Ni-Cr prime layer was deposited with a thickness of 25 nm on the pretreated LCP film using DC sputtering of a Ni-Cr alloying target, and then a Cu layer was deposited with a thickness of 100 nm, using DC sputtering of a Cu target. Both the plasma treatment and metal deposition were performed in the same chamber. After the sputtering, the specimen was subsequently electroplated in an aqueous $CuSO_4$ solution to obtain a Cu layer with a thickness of 8 μm. Fig. 3 shows a schematic description of metalizing process on the LCP film.

2.2. Characterization of modified surface and evaluation of adhesion durability

X-ray photoelectron spectra of both untreated and treated LCP surfaces were recorded with an Axis Nova Kratos X-ray photoelectron spectroscope (XPS). The monochromatic Al Kα X-ray source was operated at an anode voltage of 10 kV and at a current of 5 mA. Survey spectra were acquired from 0 to 1200 eV with pass energy of 160 eV and a step size of 1 eV. The narrow-range spectra were obtained with pass energy of 40 eV and a step size of 0.1 eV. All XPS peaks were referenced to a C1s signal at a binding energy of 284.6 eV, representing the C—C and C—H bonds in hydrocarbons.

Dynamic mechanical analysis (DMA, Q800, TA Instruments) in the film tension mode at frequency of 2 Hz and strain of 0.1%. LCP specimens had dimensions of 20 mm × 6 mm × 0.05 mm of the direction of transverse direction and machine direction, and the sample temperature was raised from −10 °C to 400 °C (5 °C/min) under a nitrogen atmosphere in order to characterize the shift with strain rate of both the α and β viscoelastic transitions of the materials.

The peel strength determined by a 90° peel at 20 mm/min. with 1 mm width with an EZ Graph (Shimadzu), is shown in Fig. 4, initial and after heating for 168 h at 150 °C in atmosphere.

After the peel test, the fracture surface on the metal and LCP surfaces were investigated with Auger electron spectroscopy (AES,

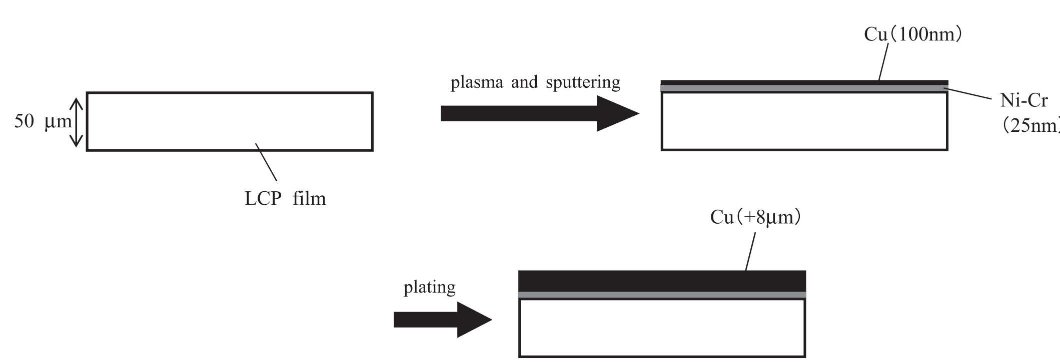

Fig. 3. Schematic diagram of the metalizing process on a LCP film.