

# Formation of conductive and reflective silver nanolayers on plastic films via ion doping and solid–liquid interfacial reduction at ambient temperature

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## Abstract

Conductive and reflective silver layers on both sides of polyimide films have been prepared by doping silver–ammonia ions into the surfaces of polyimide film, and subsequent solid–liquid interfacial reduction, during which double diffusion of silver ions and newly formed silver crystals occurred between the interfaces of polyimide films and the aqueous reducing surroundings. The newly formed silver nanoparticles could migrate and aggregate onto both sides of substrate films, forming continuous and compact silver layers that result in excellent conductivity, i.e.  $\sim 0.6$  and  $0.5 \Omega/\text{sq}$  on the upside and downside surfaces, respectively. The surface reflectivity could be detected up to 80% on the downside and 90% on the upside surface as well. The effects of the silver contents and reducing conditions on the morphologies and properties have been investigated comprehensively, and the two-side properties differences were discussed. A convective relationship between the morphologies and properties has been established, providing reliable and general guidance in terms of preparation of inorganic nanoparticles on plastic substrates. This novel and simple strategy can be extended to fabricate many other metal, metal oxide and metal sulfide nanoparticles on plastic substrates, using proper oxidants or sulfions to replace the diverse reductants. The films were characterized by inductively coupled plasma, contact angle measurement, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, four-point probe instrument and ultraviolet spectrophotometry.

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## 1. Introduction

Preparation of metal nanoparticles or nanolayers on the surface of flexible polymer substrates to endow the nanocomposite system with various optical, electrical and magnetic properties has been attracting increasing attention because of its potential applications in flexible microelectronic circuit boards, optics and outer space materials [1,2]. Various excellent performances of such nanocomposite films largely depend on the structural variability including the size, content and dispersibility of functional

nanoparticles, as well as on the physical properties of the surrounding matrix. Therefore, among all candidate polymer substrates, polyimide (PI) has been chosen due to its excellent thermal stability, special chemical bonds and structures of molecular chains that provide an additional possibility for microstructural modification and tuning of the surface properties [3–7]. Similarly, silver has been adopted as the surface functional components due to its modest cost and easy-reduced property [8], as well as high conductivity and reflectivity. The current widespread interest in surface-silvered PI nanocomposite films is largely driven by their potential applications in highly thin-film reflector concentrators in space environments for solar thermal propulsion and solar dynamic power generation,

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flexible printed circuit boards, electromagnetic interference shielding filters, optical switches, elastomeric optical mirrors, antimicrobial coating and large-scale radiofrequency antennas for space applications [9–12]. Various methods developed extensively to metallize polyimide films could be generally classified into the from-exterior-to-surface (FETS) and the from-interior-to-surface (FITS) processes. The former one includes chemical vapor deposition (CVD), physical vapor deposition (PVD), sputtering, electroplating and electroless plating [13–15]. Although these FETS processes are powerful methods to metallize polyimide surfaces, the use of the ultrahigh vacuum system and the high temperature required to vaporize the metallic phase and the poor adhesion of metal nanoparticles to matrix [16], as well as the necessity of catalytically active sites for the subsequent electroplating process, were critical hindrances to low-cost and large-scale fabrication.

To overcome such drawbacks of the FETS processes, some FITS processes were developed, which tried to grow metal nanoparticles from the interior of polyimide films. One important example was the in situ single-stage self-metallization method, during which organometallic silver complexes were firstly dissolved in desired poly(amic acid) (PAA) precursor solution, and subsequent thermal treatment converted the PAA precursor into PI matrix and reduced silver complexes species to silver nanoparticles simultaneously [9,17–21]. The adhesion between silver layers and PI substrates was strong because a mechanical interlock structure was formed [22]. However, the organometallic silver complexes were expensive and unstable when stored, and the properties of the upside and downside surfaces were different on the two sides. For clarity, the surface of the film in contact with the substrate in the commercial procedure was defined as the downside, while the surface exposed to the air was defined as the upside. Recently, our group reported another FITS process: the direct ion-exchange self-metallization technique. A simple aqueous silver solution (nitric silver) was used in this method to dope silver ions into the surface of PAA films rather than the dissolution of organometallic silver complexes in PAA solution. Subsequent thermal treatment imidized PAA to PI and reduced the doped silver ions to silver nanoparticles, which migrated to both sides of the films and formed continuous silver nanolayers on both sides [23–25]. However, all these methods mentioned above required a common condition, i.e. thermal treatment at a relative high temperature  $\sim 300\text{ }^{\circ}\text{C}$ , which would accelerate the degradation of matrix catalyzed by silver nanoparticles and even burning out the organic substrates. Besides, it was difficult to control the morphology of silver nanolayers on the surface of PI films because the thermal curing processes caused drastic aggregation of newly formed silver nanoparticles in an island growth model. Thus, a moderate reduction process that can provide the control over aggregation behavior and distribution of reduced silver nanoparticles was required.

In our previous study, we reported the chemical modification and wet reduction techniques to fabricate silver

nanolayers on PI substrates at room temperature. This method mainly relied on surface modification of PI films to form cation exchangeable sites, subsequent incorporation of silver ions via ion-exchange reactions and final reduction of the incorporated silver ions in aqueous alkali glucose solution with a relatively high pH value ( $\sim 13$ ) [26]. All processes were executed at room temperature, which would avoid the catalytic and oxidative decomposition of the PI substrates during the thermal treatment process. Moreover, the relative weak reduction capacity of the mixed solution led to moderate production of silver nanoparticles and hence reflectivity was enhanced conspicuously, and could be as high as 100% and 80% on the upside and downside surfaces, respectively. High conductivity with the minimal surface resistance of  $0.6\ \Omega/\text{sq}$  could be achieved only in the surrounding of the aqueous alkali glucose solution during the final reduction. The obtained films were detected without conductivity when it was fabricated in pure glucose solution or in the glucose solutions of alkali and with relative low pH value while the high pH solution would further hydrolyze PI substrates, which could decrease the mechanical properties of the composite films.

More recently, we reported that controllable morphologies of silver patterns on PI substrates could be achieved via an interfacial growth process, during which silver–ammonia ions served as an alternative silver resource while reductant aqueous solutions were alkali free [27]. During the final liquid–solid interfacial reduction process, double diffusion occurred, i.e. silver–ammonia ions doped in the modified layers could diffuse outward to the surface, providing a controlled and continuous supplement of silver resources for the subsequent reduction and growth process, and the reductant molecules in aqueous solution could diffuse inward to the modified layers. Silver–ammonia ions would be reduced to silver nanoparticles when they encountered reductant molecules. Aggregation behaviors of newly formed silver nanoparticles could only migrate along the liquid–solid interface that acted as the two-dimensional restrictive cues [28], and formed lamella architectures with large aspect ratio. To obtain various morphologies of these silver nanoparticles, such as fractal, cauliflower-like and microscale disks, both liquid state and solid state reducing agents were used.

Herein, the liquid state of hydroquinone was chosen as a reductant due to its weak reducing ability that favored the formation of smooth and even silver layers on PI substrates, and realization of its reducing capacity without the addition of alkali, avoiding the hydrolysis of PI substrate during the final reduction process. The effects of the silver content (hydrolysis time and ion-exchanging time) and reducing conditions (concentration, temperature and time) on the morphologies and properties have been investigated comprehensively, and a convictive relationship between the morphologies and properties has been established which provides reliable and general guidance in terms of preparation of inorganic nanoparticles on plastic surfaces. Because of the convenience of the procedure

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