CHAPTER II

BACKGROUND INFORMATION

2.1 Polyimide

Polyimide (PI) is a polymer of imide monomers. The structure of imide usually takes one of two forms (see in Figure 2.1). The first form is a linear structure, in which atoms of the imide group are part of a linear chain. The second form is a heterocyclic structure, in which the imide group is part of a cyclic unit in the polymer chain.

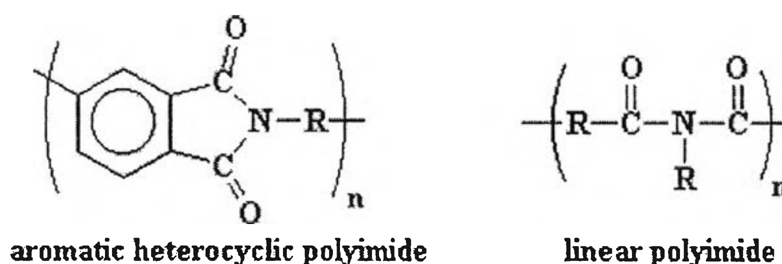

Figure 2.1 Polyimide structures.

Polyimide is synthesized by polymerizing an aromatic dianhydride with an aromatic diamine. It has excellent chemical resistance such that there is no known organic solvent for PI. It does not melt. It can be used at both high and low temperature extremes. Kapton® polyimide films can be used in a variety of electrical and electronic uses, e.g. wire and cable tapes, formed coil insulation, substrates for printed circuit boards, motor slot liners, magnet wire insulation, transformer and capacitor insulation, magnetic and pressure-sensitive tapes, and tubing.

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Table 2.1 Properties of polyimide (Kapton® 100HA).

Properties	
Mechanical properties	
Tensile strength, psi (MPa)	33,500
Ultimate elongation, %	72
Tensile modulus, psi (GPa)	370,000
Electrical properties	
Dielectric strength, V/mil (kV/mm)	7700
Dielectric constant at 1 Khz	3.4
Dissipation factor at 1 Khz	0.0007
Electrical resistivity	1.00×10^{10} ohm-cm
Thermal properties	
Glass transition temperature	>400°C

2.2 Silver

Silver has been known since prehistoric time and was discovered soon after the discovery of gold and copper. Silver was considered to be a precious metal although it was not as important or highly looked up on as gold, but it was still used cautiously. Silver is very ductile and malleable and because of these properties, as well its luster, silver was mainly used for ornamental purposes in ancient times.

Pure silver is nearly white, lustrous, soft, very ductile, and malleable. It is an excellent conductor for both heat and electricity (see Table 2.2). It is not a chemically active metal, but it is attacked by nitric acid (forming the nitrate) and by hot concentrated sulfuric acid. It has the highest electrical conductivity among all metals, but its greater cost has prevented it from being widely used for electrical purposes. Silver is almost always monovalent in its compounds, but an oxide, a fluoride, and a sulfide of divalent silver are known. It does not oxidize in air but reacts with the hydrogen sulfide present in the air, forming silver sulfide (tarnish). Silver is stable in water.

Table 2.2 Physical properties of silver.

Properties	
Atomic mass average	107.8682
Boiling point	2436K 2163°C 3925°F
Density	10.5g/cc @ 300K
Conductivity	
Electrical	0.63 10^6/cm Ω
Thermal	4.29 W/cm K

2.3 Hydrolysis of polyimide

Hydrolysis of polyimide is mostly used to convert polyimide to polyamic acid (Thomas et al., 1992; Faupel et al., 1998; Wu et al., 2005) by cleaving the imide ring into carboxylic and amide groups (see Figure 2.2).

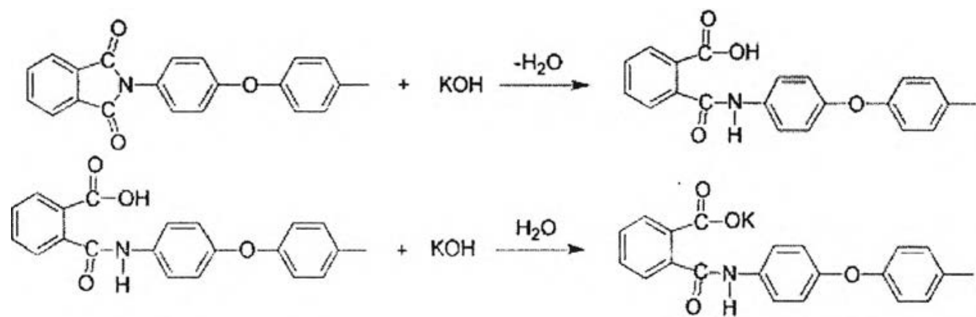

Figure 2.2 Imide ring opening in polyimide film by KOH treatment.

Carboxylic groups, i.e. poly(amic acid), obtained after hydrolysis improves hydrophilic property of the surface by increasing polar component of surface energy as reported by Park et al. (Park et al., 2007). KOH treatment introduces carbon-oxygen functional groups onto the surface of polyimide. The O1s/C1s ratio of the KOH-treated polyimide has been reported to increase as a function of the treatment time, resulting in enhancing surface free energy.

Increasing adhesion of PI surface can be obtained by increasing time in hydrolysis process as reported by Yoon et al. (Yoon et al., 2008). The effect of the

KOH treatment on the surface characteristics of the polyimide could be witnessed from the decrease in the contact angle with the increase in KOH treatment time. After the drastic drop within the first 1 min, the contact angle remains fairly constant, demonstrating that the chemical structure of the polyimide was quickly changed within the first 1 min of KOH treatment. Although the chemical structure of the polyimide surface was completely modified within 1 min, the modification depth further increased with the treatment time. However, if the treatment time is prolonged, PI film would decompose as reported by Hsiao et al. (Hsiao et al., 2008) that extended KOH treatment could further increase the proportion of cleaved imide rings, but the PI film would become warped and crooked at high cleaved imide content. The best PI film for the following surface-nickelized treatments was obtained by treating KOH for 30 min.

2.4 Impregnation of metal ions into polyimide

Poly(amic acid) have significantly higher cation-complexing properties than their imide forms due to the presence of many active carboxylic acid groups within the macromolecules. This characteristic allows in-situ reactions with salts of noble metals having labile anions to generate metal-polymeric blend (Andreescu et al., 2005). Silver ions can be successfully introduced into the poly(amic acid) films by ion exchange in aqueous silver(I) solutions. It has been suggested that the metal ions were loaded through the coordination of the negatively charged polycarboxylate groups with the positive silver ions to form silver polycarboxylate salt and silver polyamate in the precursor films. However, the efficiencies of incorporating metal ions using silver nitrate and silver fluoride were rather disappointing, i.e. the silver(I) solution must have high concentration (Qi et al., 2008).

To load metal ion into polyimide surface (see Figure 2.3), temperature, concentration and pH of the solution (electrolyte) play important role to control amount of metal ion adsorbed on polymer surface. Akamatsu et al. (Akamatsu et al., 2003) reported that copper ion loading could also be controlled by changing pH of the $CuSO_4$ solution. The decrease in pH for the ion exchange reaction resulted in significant decrease in Cu^{2+} adsorption, suggesting that pH could be varied to control

the amount of copper ions adsorbed onto the modified PI layer, in which the thickness was determined by initial KOH treatment. Although the maximum amount of adsorbed Cu^{2+} ions essentially depended on the number of carboxyl groups formed, it was demonstrated that the Cu^{2+} ion loading in the film could be systematically controlled by varying experimental conditions.

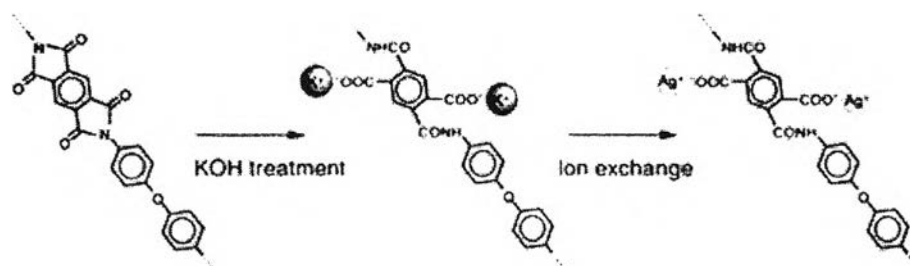

Figure 2.3 Loadings of adsorbed potassium ions in a polyimide film.

2.5 Photo reduction of metal ion

The oxidation state of the metal in a transition metal complex can change, leading to reduction-oxidation (redox) processes. Most transition metal ions can form complexes with many types of organic ligands or water. Many transition metal ions with low oxidation states can react with molecular oxygen, mediating the oxygenation of other compounds. The complexes of these metal ions in their higher oxidation states can be reduced to their lower oxidation states by electron transfer (Wang et al., 2004).

The UV-light-induced reduction of silver ions is a water-accelerated process, similar to the aqueous-solution-based formation of silver colloids. Possible reaction mechanisms for the formation of Ag nanoparticles are:

$$\text{-COO}^- + Ag^+ \xrightarrow{h\nu} \text{-COO}^\bullet + Ag^0 \qquad (1)$$

$$n(Ag^0) \longrightarrow (Ag^0)n \qquad (2)$$

UV induced reduction of silver ions can be initiated by charge transfer from the carboxylate ions to silver ions, resulting in the formation of carboxyl radicals and silver atoms. The reduction of silver ions therefore occurs predominantly near the

surface of the modified layer in the early stage of irradiation (Akamatsu et al., 2003). The silver crystal are kept at the interface and the overall rate of silver deposition is limited by the low concentration of silver in the aqueous phase (Scholz and Hasse 2005).

2.6 Growth of silver cluster

Silver clusters can grow to many tens of nanometers in diameter and thickness. Uncovered active regions undergo electron migration, due to the excitation from the UV, to the surface and allow the clusters to continue growing. As the edges of the clusters grow, the exposed surface area is decreased as it is shadowed from the UV by the clusters. When the edges of the clusters meet the electron migration stops (Jones and Dunn 2007).

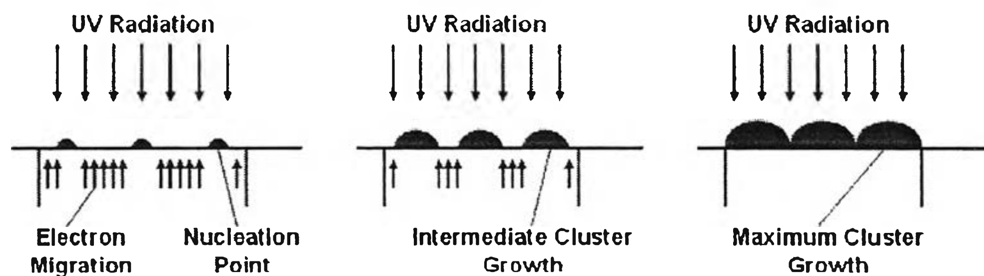

Figure 2.4 Ag cluster growth retardation mechanism.

The clusters grow in a pseudo semi-hemispherical manner as electrons are able to migrate through the silver thereby generating negative charges on the surface of the silver as well as at the edges of the growing cluster. This migration of electrons is random in nature so that there is an equal chance of the cluster growing in the x, y, z directions.

2.7 Sintering of silver nanoparticles

The changes in metal film thickness as well as the sheet resistance arise from sintering, which is a material transport process based on atomic diffusion driven by the reduction of interfacial energy. Schematic representation of possible diffusion paths during sintering between two particles is shown in Figure 2.5.

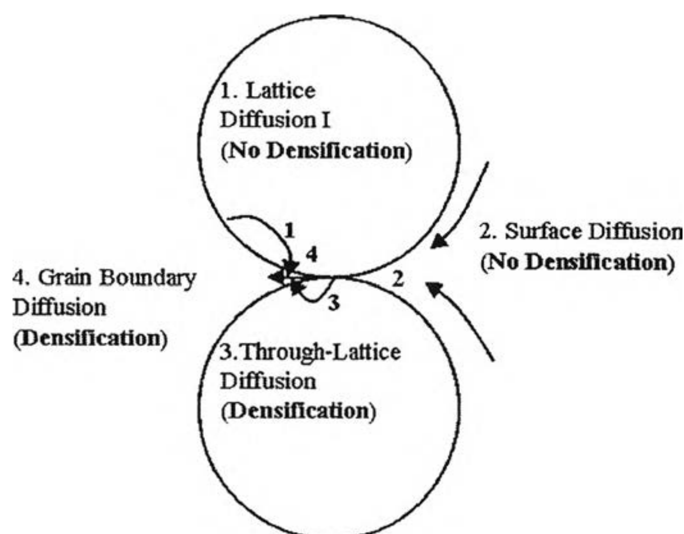

Figure 2.5 A scheme representing various atomic diffusion paths between two contacting particles.

Paths 1 and 2 correspond to surface and lattice diffusion, respectively. These mechanisms do not cause densification, since no change in distance between the sphere centers occurs. In crystalline materials, shrinkage, and therefore densification, can occur only when the atoms are removed from the contact surface, or a grain boundary, so that the centers of the spheres can move towards one another (Paths 3 and 4). In these processes, the centers of spherical particles approach one another, as the neck between them widens, increasing the particle contact area. The neck formation is also driven by the reduction in surface energy by atomic diffusion, where the material fluxes from the areas of convex or positive curvature to the regions of negative, curvature, or concave. The energy reduction by neck formation is offset by the energy of grain boundary creation, and this energy balance dictates the final shape of the pore. These atomic diffusion processes compete with each other. For example, surface diffusion generally prevails in the initial sintering stages, as it has the easiest transport path as well as low activation energy. While the atomic mobility within a grain boundary is much higher than that in the lattice, it can not accommodate a large number of atoms, so the atomic flux in the very thin grain boundary is much lower compared with that in the lattice. The activation energy for grain boundary diffusion is much lower than that for lattice diffusion, making the former prevail in the initial stages of sintering, when densification is minimal, and the latter at high temperatures, when most shrinkage occurs. One of the key factors determining the dominant transport mechanisms is the initial particle or grain size. The smaller the grain, the

larger the volume fraction occupied by the grain boundary. The kinetics of sintering are complex, as they depend on which of these transport mechanisms are dominant (Greer and Street 2007).

2.8 Electroless plating

Electroless plating is a chemical reduction process which depends upon the catalytic reduction of metal ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of metal without the use of electrical energy. Due to the exceptional corrosion resistance and high hardness of the plated film, the process finds wide application on items such as valves, pump parts etc., to enhance the life of components exposed to severe conditions of service, particularly in the oil field and marine sector. With correct pretreatment sequence and accurate process control, good adhesion and excellent service performance can be obtained from electroless plating deposited film on a multitude of metallic and non-metallic substrates.

In the electroless plating process, the driving force for the reduction of metal ions and their deposition is supplied by a chemical reducing agent in solution. This driving potential is essentially constant at all points of the surface of the component, provided the agitation is sufficient to ensure a uniform concentration of metal ions and reducing agents. Electroless deposits are therefore very uniform in thickness all over the part's shape and size. This process offers distinct advantages when plating irregularly shaped objects, holes, recesses, internal surfaces, valves or threaded parts

2.9 Chemical reduction by ($NaBH_4$).

The borohydride reducing agent may consist of any water soluble borohydride compound. Sodium borohydride is generally preferred because of its availability. Substituted borohydride in which not more than three of the hydrogen atoms of the borohydride ion have been replaced can also be used.