Defects Suppression of Ni-P thin Film on Polymer Substrate via catalyzation in Sc-CO_2 and Electroless Plating in Sc-CO_2 emulsion

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1. INTRODUCTION

The flexible and biocompatible properties of polymer make polymer MEMS promising candidates for the next generation of micro devices. Bio-medical micro devices such as intracortical electrode on polymer substrate for neural interface are envisioned[1-2]. Polyimide has many outstanding properties, including good thermal stability, low dielectric constants, low dissipation factors, and inherent surface inertness. In addition, the polyimide surface chemistry is amenable to modifications and preparations which allow a host of bioactive organic species to be either adsorbed or covalently bonded to its surface[3]. These properties are important for application in MEMS technology. The best way to improve the quality of the metallization on polymer will be to develop a novel micro-fabrication technique for plating metal onto polymer substrate. Electroless plating were widely used for making thin film on organic substrate. Yet polymer substrates are hydrophobic and respond poorly to the wetness of the electroplating solution. One way to achieve contact Pd catalyzation on polymer substrate under this condition is to change from a hydrophobic to a hydrophilic surface. Chromate treatment has been used for this purpose in conventional catalyzation, but the environmental affinity restricts the applicability[4]. To alleviate this problem, we proposed a novel technique which is carried out in Sc-CO_2 with organic Pd complex in catalyzation procedure and an electroless plating reaction are conducted in emulsion of Sc-CO_2 and electroless plating solution with surfactant[5]. In previous experiment, we obtained an Ni-P thin film with fewer pinholes and voids by catalyzing the polyimide using supercritical CO_2 and an electroless plating mixing emulsion. Moreover, we discussed Sc-CO_2 effect on nucleation and nuclei growth of catalyst for uniform and smooth metallization on polymer through quantitative microscopic method on the microscopic images of the catalyzed substrates and the plated films with comparison with conventional catalyzation[6-7]. However, the problems to solve which individual properties of Sc-CO_2 play a dominant role to suppress the defects are remained. If we are to use this method, we must clarify effects of Sc-CO_2 for suppression of voids on electroless plated thin metal film and improvement of interface stability between fabricated metal and polymer substrate. In

this report, we discuss how transport properties of Sc-CO_2 and the affinity with substrate affect the suppression of the defects in Ni-P thin film on polyimide substrate.

2. MATERIALS AND METHODS

Carbon dioxide with a minimum purity of 99.9% was purchased from Nippon Tansan Co., Ltd. A small amount (300μl) of polyoxyethylene lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{15}OH$) was used as a nonionic surfactant for the mixing of the electroless plating solution with Supercritical Carbon dioxide (Sc-CO_2). The chemical compositions of Ni-P plating solution were reported in previous report[5]. A square sheet of polyimide Kapton © (1.0 x 2.0cm^2 ; thickness, 130μm) was used as the substrate. Figure 1 shows the high-pressure experimental apparatus (Japan Spectra Company). The reaction chamber was a stainless steel 316 vessel with a volume of 50 ml. Three kinds of catalyzation procedure were performed. In conventional catalyzation, the polyimide substrate was immersed in a mixed $PdCl_2$/ HCL solution (0.04% $PdCl_2$ and 18% HCl) for 20 min and washed with HCl. Secondly, immersion of the polyimide substrate in Sc-CO_2 for catalyzation, Pd bis-acetylacetonate (concentration: $1.219x10^{-6}$ mol/L) was deposited onto the substrate in Sc-CO_2 for 20 min. The reaction temperature and pressure were 353 K and 15 MPa, respectively. Thirdly, catalyzation procedure were performed in Hexanee solvent (40ml) with 0.25g Pd-acetylacetonate for 20min reaction time on 353K. Catalyzed polymer substrates were plated in Ni-P electroless solution by two types of electroless plating reaction. Two kinds of electroless plating were performed. In the conventional electroless plating, catalyzed polyimide substrate was immersed in an Ni-P electroless plating solution and then an Ni-P thin film was fabricated. The electroless plating in the emulsion of CO_2 in Ni-P electroless solution was conducted at 353 K and 15 MPa. An optical microscope (Digital Microscope VHX-500, KEYENCE. CO., Ltd) and scanning electron microscope (FE-SEM, S-4500, Hitachi High Technologies Co., Ltd) were used to observe the surfaces of the plated Ni-P films.

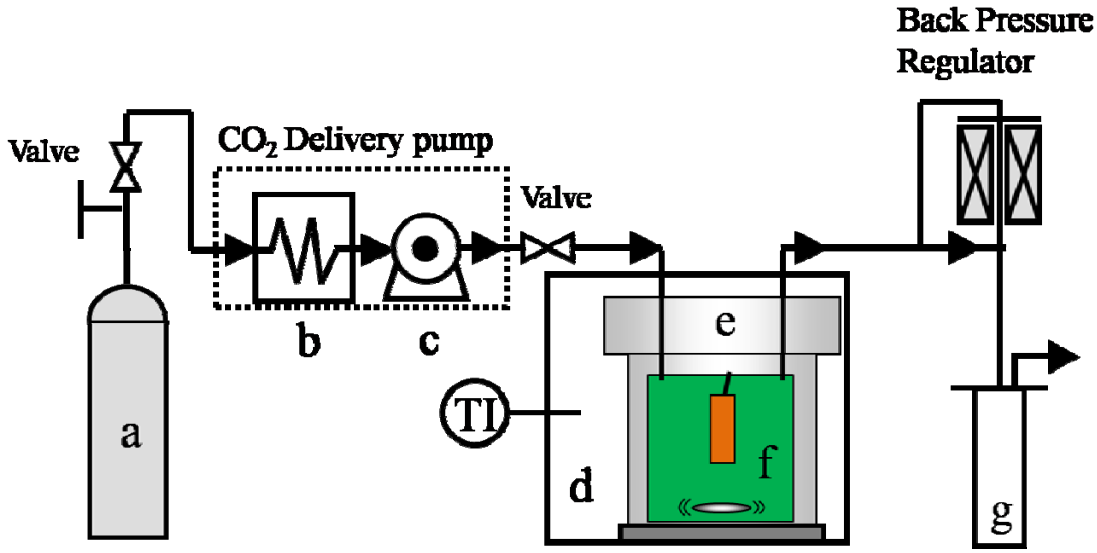
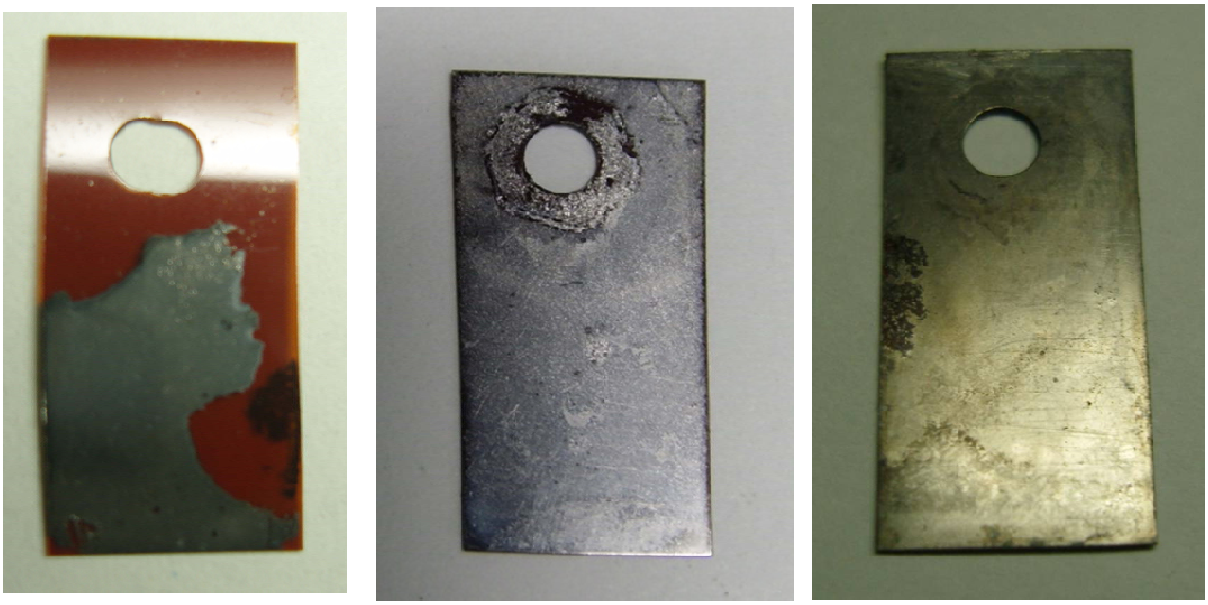


Figure 1. (a) CO_2 gas tank, (b) liquidization unit, (c) high pressure pump, (d) thermal bath (e) reaction cell, (f)stirrer + substrate + Supercritical CO_2, (g) trap , TI：thermometer,

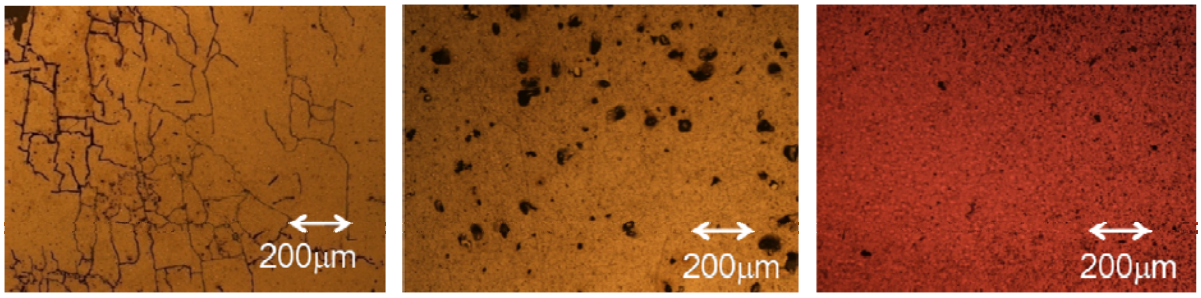


(a) (b) (c)

Figure 2. Photographic images of electrolessly plated polyimide after conventional catalyzation for 20 min (a), Ni-P thin film by electroless plating for 20min on Sc-CO_2 catalyzation for 20 min (b) and Ni-P thin film using supercritical CO_2 and an electroless plating mixing emulsion for 20 min after Sc-CO_2 catalyzation for 20 min (c).

3. RESULTS AND DISCUSSION

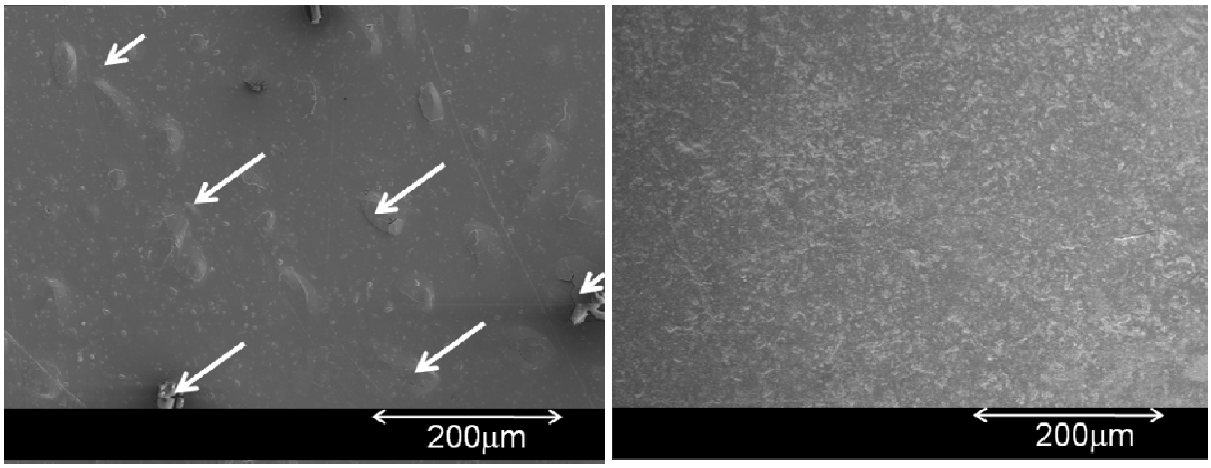
Figure 2 shows the partially plated Ni-P on polyimide substrate and the substrates electrolessly plated with Ni-P by different methods. Fig. 2(a) show partially coated Ni-P thin film on polyimide substrate with conventional catalyzation. The meager nucleation on the hydrophobic polyimide surface apparently impeded conventional electroless plating after conventional catalyzation. But, Figs 2(b) and (c) show totally plated Ni-P thin film. Sc-CO_2 catalyzed polyimide substrate was immersed in the Ni-P electroless plating solution, the entire substrate surface was plated with Ni-P thin film. According to these results, we concluded that catalyzation procedure using Sc-CO_2 have effects on the nucleation and nuclei growth of catalyst toward uniform and smooth metallization on polymer by electroless pla ting, in comparison with the effects in conventional catalyzation. Figure 3 shows optical microscopic images of electrolessly plated Ni-P thin film surface. First, conventionally plated Ni-P film (a) were lots of cracks. Ni-P thin film with electroless plating for 20 min after Sc-CO_2 catalyzation for 20 min (b) were lots of pin-holes and peeled parts. However Ni-P thin film using supercritical CO_2 and an electroless plating mixing emulsion for 20 min after Sc-CO_2 catalyzation for 20 min(c) were conformal and less defects on film. The electroless plated Ni-P thin films treated by Sc-CO_2 catalyzation are free of cracks and were deposited over the entire surface. The cracks in the former film are suggested to result from the low cata lyst density and poor uniformity of the catalysts on the polyimide substrate. Figure 4 shows an SEM image of a Ni-P thin film surface after Sc-CO_2 catalyzation of conventional electroless plating(a) and Ni-P thin film surface using Sc-CO_2 and an electroless plating mixing emulsion after Sc-CO_2 catalyzation (b). Figure 4(a) show numerous defects such as peeled sections and nodules on the Ni-P thin film.



(a) (b) (c)

Figure 3. Optical microscopic images of electrolessly plated Ni-P thin film on polyimide after conventional catalyzation for 20 min (a), Ni-P thin film by electroless plating for 20 min on Sc-CO_2 catalyzation for 20 min (b) and Ni-P thin film using supercritical CO_2 and an electroless plating mixing emulsion for 20 min after Sc-CO_2 catalyzation for 20 min (c).

The peeling resulted from the hydrogen bubbles generated by the sub-reaction of the electroless plating on the polyimide substrate. In the conventional electroless plating, the hydrogen gas generated by the sub-reaction led to the formation of pinholes and voids on the Ni-P thin film. However Figure 4(b) shows that process resulted in a uniform thin film without peeled sections on the view point of macroscopic property and porosity. These results come from that Sc-CO_2 dissolves hydrogen gas and thus decreases the peeling in supercritical electroless plating[5,9]. Supercritical CO_2 has high miscibility with hydrogen. This leads to the dissolution of the generated hydrogen in Sc-CO_2 and thus decreases the peeling on the polyimide substrate. According to experimental results, Sc-CO_2 has good effects on both catalyzation and electroless plating. We suggested that Sc-CO_2 has two major effects to suppress defects on Ni-P thin film on polyimide substrate. First, Sc-CO_2 has good chemical affinity with polyimide substrate for deposition of catalysts. Secondly Sc-CO_2 has high diffusivity property which transports Pd-catalyst into inside of polymer. In order to clarify which property plays a dominant role to suppress defects, we selected hexane for catalyzation solvent. Hexane is known to have similar solvent properties to Sc-CO_2 [8].



(a) (b)

Figure 4. SEM images of Ni-P thin film using conventional electroless plating on Sc-CO_2 catalyzation for 20 min (a), Ni-P thin film using Sc-CO_2 and an electroless plating mixing emulsion for 20 min on Sc-CO_2 catalyzation for 20 min(b).

Especially, it was reported that Hexane has same electrochemical properties of emulsion such as current conductivity, the resistances and the current efficiencies of Sc-CO_2 emulsions, due to no dipole moment[10]. But Sc-CO_2 diffusion coefficient with polymer is about 10000 times larger than Hexane [11-12]. We fabricate Ni-P thin using supercritical CO_2 and an electroless plating mixing emulsion after catalyzation in hexane. Figure 5 shows images of optical microscope and SEM of Ni-P thin film using Sc-CO_2 and an electroless plating mixing emulsion after catalyzation in Hexane. Comparing with Fig.4(b), lots of cracks were observed on Ni-P thin film. These cracks are suggested to come from low density of catalyst on polymer substrate [7]. Moreover, our previous study clarified that, in case of Ni-P thin film using Sc-CO_2 and an electroless plating mixing emulsion after Sc-CO_2 catalyzation, the penetrated Ni peaks were observed at a depth of 170 nm inside the polyimide substrate by EDX analysis[5]. These penetrated Ni-P atoms can affect defects of Ni-P surface. In catalyzation in hexane media, Pd catalysts were deposited only on polyimide surface but not inside of polymer and also Ni-P metals were grown only on polyimide surface but not from inside of polymer. On the other hand, Sc-CO_2 makes Pd nucleates at a depth of 170 nm through Sc-CO_2 catalyzation procedure. Moreover, in electroless plating procedure, the high diffusivity properties of Sc-CO_2 make Ni-P electroless plating solution to penetrate polyimide substrate. These penetrated Ni-P particles play a role to anchor between Ni-P thin film and polyimide substrate toward good interface stability. According to these result, both the enough density of catalysts and Ni-P metal growth in depth direction of surface of polymer substrate must be essential for suppression of cracks.

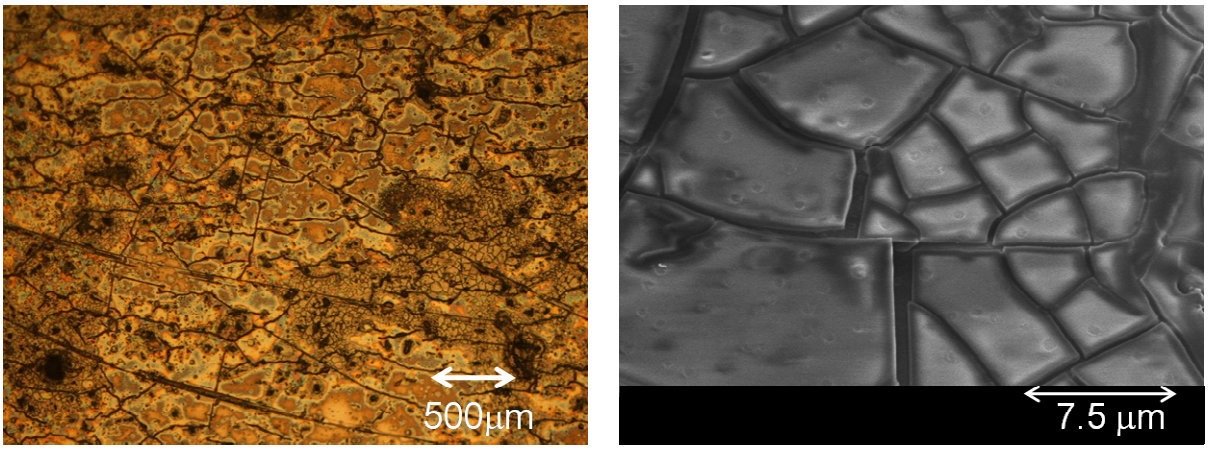


Figure 5. Optical microscopic image (a) on Ni-P thin film and SEM images(b) on Ni-P thin film using Sc-CO_2 and an electroless plating mixing emulsion after catalyzation in Hexane.

4. CONCLUSION

We have proposed a novel metallization technique onto polymer, which catalyzation procedure is carried out in Sc-CO_2 with organic Pd complex and then an electroless plating reaction are conducted in emulsion of Sc-CO_2 and electroless plating solution with surfactant. This novel technique can form an Ni-P thin film with fewer pinholes and voids. We studied how transport properties of Sc-CO_2 and the affinity with substrate to suppress the defects of Ni-P thin film on polyimide substrate. In catalyzation procedure, good chemical affinity between polymer and Sc-CO_2 could induce the Pd bis-acetylacetonate to disperse over all of the surface-treated polyimide, thus facilitating uniform catalyzation growth. The abundance of catalyst nuclei facilitated the deposition of the Ni-P thin film onto the

polyimide substrate. Moreover, Pd catalyst nucleated at a depth of 170 nm in Sc-CO_2 catalyzation procedure due to the high diffusivity property of the Sc-CO_2. In electroless plating procedure, Ni-P thin films with fewer pinholes and voids were obtained with high solubility properties of Sc-CO_2 with hydrogen gas. The high diffusivity properties of Sc-CO_2 made Ni-P electroless plating solution to penetrate polyimide substrate. This Ni-P metal growth in depth direction can make suppress the cracks on Ni-P thin film.

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