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Electroless nickel plating on patterned catalytic surfaces by electron beam lithography

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Abstract

Nickel–phosphorus (Ni–P) alloy thin films with high-resolution features were created on patterned palladium (Pd) catalytic surfaces by electroless plating. Pd catalyst underlayers were patterned by incorporating Pd nanoparticles with site selectivity into poly(methyl methacrylate) thin films by combining electron beam lithography and the reduction of palladium(II) bis(acetylacetonato) used as a precursor. The quality of the metallic surface patterns was evaluated in terms of the attainable pattern sizes and the deviation from the pre-designed patterns. Dense Ni–P lines with the width of about 150 nm could be obtained with good site selectivity.

Keywords: Electroless plating; Electron beam lithography; Patterning; Nickel; Palladium

1. Introduction

With increasing demands for mass production of metal or metal oxide thin films with high-resolution features, electroless plating technique has been combined to various patterning techniques, such as electron-beam (E-beam) lithography [1,2], photo lithography [3,4], nanoimprint lithography [5,6], soft lithography [7–9], nanosphere lithography [10,11], and so forth. Electroless plating has the following advantages as a deposition technique: (1) it is a simple and economical low-energy process without external power sources; (2) it allows us to make mass production of uniform thick coatings on various substrates with regardless of their conductivity; (3) it can be applied to the complex and hardly-accessible three dimensional surfaces; and (4) the deposited thin films and the substrates are safe from the thermal stress because the process is performed under mild conditions.

In order to perform electroless plating, a substrate surface must be catalyzed prior to the plating. Traditionally, the sensitization and the subsequent activation process by using $SnCl_2$ and $PdCl_2$ aqueous solutions, respectively, has been employed, where palladium (Pd) nanoparticles are produced by the reduction of $PdCl_2$. Sugimura et al. [12] reported the possibility of nickel patterning on the UV-patterned Pd catalysts fabricated using a self-assembled monolayer (SAM), in which the catalysts were produced in $PdCl_2$/HCl/HF solutions. Dressick et al. [13] demonstrated selective entrapment of pyridine on the *p*, *m*-chloromethylphenyl–trichlorosilane and polyvinylvenzyl chloride film, where the nitrogen atom of the entrapped pyridine adsorbs Pd catalyst by immersion to a colloidal Pd(II) solution. Saito et al. [14] fabricated an electroless ZnO micropatterns on the Pd catalyst fabricated using a photo-patterned phenyltrichlorosilane SAM.

We have developed, on the other hand, a simple and easy dry process to introduce Pd nanoparticles into polymer thin films *via* the reduction of palladium(II) bis(acetylacetonato), Pd $(acac)_2$ [15–20]. Particularly, we have found that reducing power of poly(methyl methacrylate), (PMMA), can be largely strengthened by the irradiation of UV light or E-beam prior to the exposure to $Pd(acac)_2$ vapor, which enables the patterning of the Pd-catalyst layer on substrates by photolithography or E-beam lithography techniques [19,20]. We have reported the site-selective electroless deposition of ZnO nanocrystals on the photo-patterned Pd-catalyst surfaces [20].

As reported in our previous papers [15,16], PMMA exhibits a unique behavior in terms of the absorption and the reduction of the $Pd(acac)_2$ vapor. $Pd(acac)_2$ in vapor state can be absorbed

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in a PMMA film, but the reduction of $Pd(acac)_2$ is retarded, resulting in the suppression of the formation of Pd nanoparticles, while most of other polymers can reduce $Pd(acac)_2$ simultaneously. However, the PMMA chains decomposed by E-beam or UV light can accelerate the reduction of $Pd(acac)_2$ and the formation of the Pd nanoparticles. Therefore, the Pd nanoparticles can be assembled in a PMMA thin film into the regions irradiated by UV light or E-beam.

The Pd nanoparticles thus introduced in polymer thin films exhibit an excellent catalytic activity for the electroless deposition. We have reported that the ZnO nanocrystals could be deposited from the aqueous solution comprising of $Zn(NO_3)_2$ and dimethylamineborane onto the PMMA surface enriched with the embedded Pd nanoparticles [20]. Therefore, the microscale patterns of ZnO nanocrystals could be constructed by UV photolithography.

In this study, we attempted to reduce the pattern feature sizes of deposited metallic films into nanometer ranges by E-beam lithography through the investigation of the electroless nickel plating. Nickel coating has been widely used for electronics components and electromagnetic interference shielding because of its solderability, high diffusion barrier resistance, and low electrical resistance [21]. When sodium phosphonate monohydrate ($NaPH_2O_2 \cdot H_2O$) is used as a reducing agent, phosphorus atoms are incorporated into nickel films, forming Ni–P alloy deposits [22]. Electroless Ni–P coatings with low phosphorus content possesses ferromagnetism and high wear resistance, which enables to produce thin film magnets and microactuators [1,23]. Therefore, the possibility of patterning of Ni–P films in nanometer scales could lead to a variety of electronics applications. We evaluated, in this study, the patterning of Ni–P plated films in terms of the pattern feature size and the deviation from the defined Pd-catalyst patterns.

2. Experimental section

2.1. Materials

$Pd(acac)_2$ was purchased from Johnson Matthey Materials Technology and was recrystallized in acetone. PMMA was obtained from Aldrich Chemical Co., Inc. whose number-average molecular weight was 350,000. It was precipitated twice from methylene chloride into methanol for purification before use. Nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), $NaPH_2O_2 \cdot H_2O$, lactic acid ($CH_3CH(OH)COOH$), and propionic acid (CH_3CH_2COOH) were used as received from Wako Pure Chemical Industries, Ltd.

2.2. Preparation of Pd patterns by E-beam and UV lithography

PMMA thin films with 80 nm thickness were spin-coated on a cleaned Si(100) wafer from 2.0 wt.% toluene solution and the

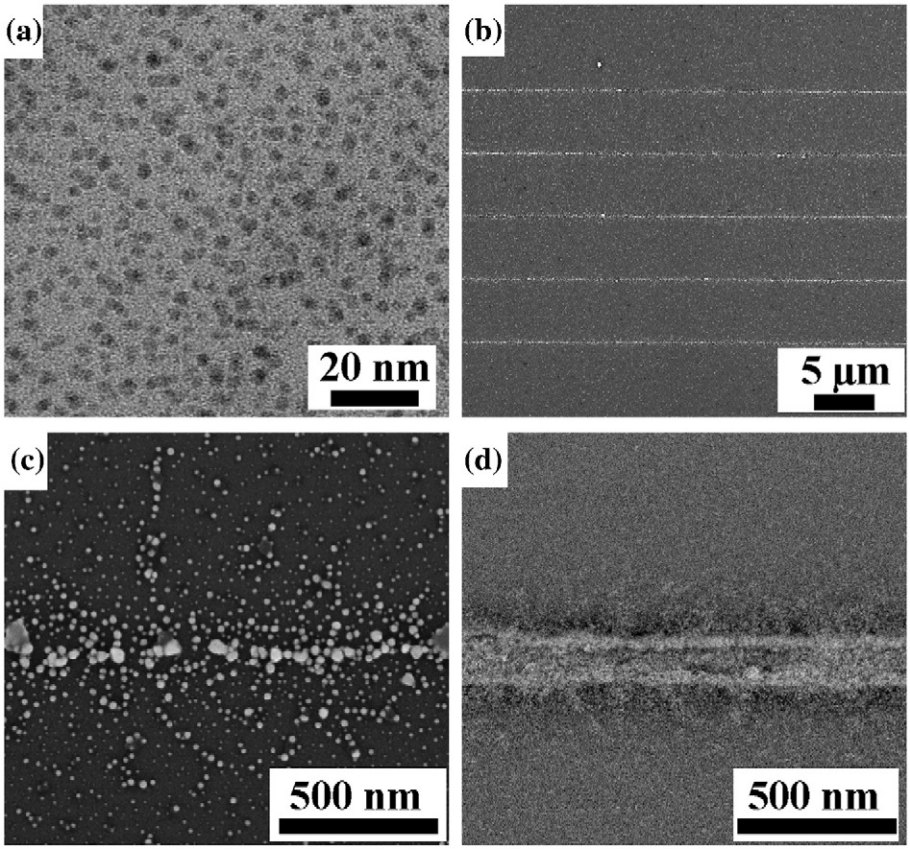

Fig. 1. (a) TEM micrograph showing uniformly distributed Pd nanoparticles in the PMMA thin film. (b) SEM micrographs showing Pd-catalyst pattern prepared by E-beam lithography after pyrolysis of the PMMA film at 550 °C for 30 min in Ar gas flow. (c) is an enlarged view of (b). (d) SEM micrograph showing Pd-catalyst pattern after stripping the PMMA film by rinsing with acetone for 3 min.