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RESEARCH ARTICLE

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Method for Patterning Various Nanomaterials: Electrochemical Deposition of Patterned Ni Thin Films and Their Utilization as a Strippable Mask

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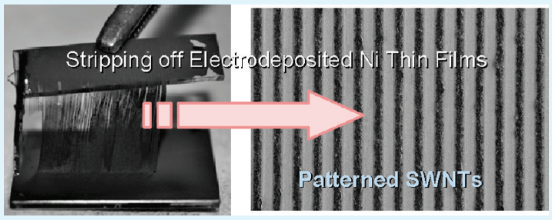
ABSTRACT: We report an interesting approach for preparing micro-patternings of nanomaterials, such as carbon nanotubes and TiO_2 nanoparticles. In the method, exfoliation of electrodeposited Ni thin films was the key process. After patterning indium thin oxide (ITO) plates with an insulating photoresist by conventional photolithography, Ni was electrodeposited on only the exposed ITO areas. The resulting substrates were evenly covered with nanomaterials by a drop cast method. By exfoliating the electrodeposited Ni thin films from the substrates, patterned nanomaterial films were formed.



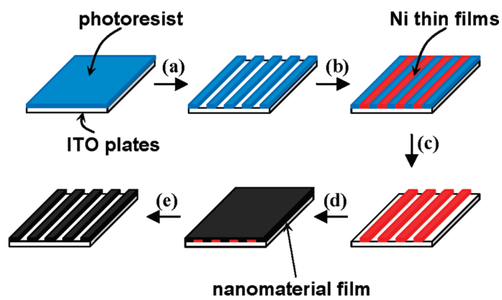
KEYWORDS: micropatterning, carbon nanotubes, nanoparticles, electrodeposition, metal−metal oxide interface

INTRODUCTION

The development of a reliable method for patterning nanomaterials is an interesting issue because patterned nanomaterials are expected to be used in various fields such as microelectronics, energy storage, sensors and displays.[1−3] For example, the fabrication of patterned carbon nanotube (CNT) films has been vigorously investigated due to extraordinary chemical, electrical and mechanical properties of CNTs.[4] The fabrication techniques of patterned CNT films are roughly classified into two methods: direct growth method and wet-deposition method. In direct growth method, chemical vapor deposition (CVD) is the most common process, in which prepatterned metal nanoparticles are used as catalysts for CNT growth.[5−7] In contrast, wet-deposition methods are low temperature processes and do not need a high-vacuum system, which reduces costs significantly. In most wet-deposition methods, many chemical approaches (e.g., inkjet printing,[8] microfluidic channel guided coating,[9] and the utilization of chemical interactions or difference in surface energy[10−13]) are developed to assemble CNTs in desired location. In addition, not just CNTs, but other nanomaterials such as nanoparticles are also expected to be used as patterned films because nanomaterials show different properties from bulk material.[14−16] However, the methods to prepare patterned CNT films cannot be simply applied for other nanomaterials, because CVD is the specialized method for CNT growth, and most of the wet-deposition methods to pattern CNTs are based on inherent chemical or physical properties of CNTs. Therefore, to pattern a certain nanomaterial, the preparation approach has to be designed based on chemical or physical natures of the nanomaterial, that is, individualized approaches are needed to pattern diverse nanomaterials.

In this study, a wet-deposition method to pattern diverse nanomaterials was developed. We propose a novel approach in which patterned Ni thin films that are electrochemically deposited are utilized as a strippable mask. The method consists of two conventional techniques: photolithography and electrochemical deposition. The schematic diagram of the method is shown in Scheme 1. First, an insulating photoresist film was patterned on indium thin oxide (ITO) plates by conventional photolithography (Scheme 1a), and then patterned Ni films were electrodeposited on the exposed ITO lines by the electrochemical reduction of Ni^{2+} ions (Scheme 1b). After removal of the photoresist layers, nanomaterial dispersion was casted on the substrates, forming nanomaterial coatings (Scheme 1c and 1d). Here we focused the low adhesion force between metals and metal oxides (in this study, Ni and ITO). Generally, adhesion force between an electrodeposited metal thin film and a metal oxide substrate is low, because internal stress is often induced due to the misfit of their crystal structure or lattice constant; therefore, it is expected that electrodeposited metal thin films can be readily stripped off from

Scheme 1. Schematic Diagram of the Fabrication Process for Patterned Nanomaterials: (a) Photolithography, (b) Electrochemical Deposition of Ni Thin Films, (c) Removal of Photoresist Layers, (d) Coating of Nanomaterials, and (e) Stripping off Ni Thin Films



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metal oxide substrates. In our case, as shown in Scheme 1e, it is expected that the patterned Ni films could be stripped off from the ITO plates, and the nanomaterials on the Ni films are also removed. As a result, the remained nanomaterials would form patterns that reflect the shapes of the photoresist patterns, that is, we could use the patterned Ni thin films as a strippable mask to pattern nanomaterials. In this method, surface nature, size, shapes and structure of nanomaterials do not have any influence to form patterns. Thus, the method would be able to apply to pattern diverse nanomaterials.

So far, especially in electronic field, patterned metal thin films have been focused on and prepared by electroless deposition method.[17] However, as far as we know, it is the first report that electrodeposited metal films are utilized as a strippable mask in material design fields.

EXPERIMENTAL SECTION

Photolithography. Indium tin oxide (ITO) plates with a size of 25×20 mm^2 (Kinoene kogaku kogyo Co., Ltd.) were washed under ultrasonic radiation in acetone for 10 min, and then in ethanol for 10 min. They were baked at 343 K for 5 min. After a solution containing hexamethyldisilazane (OAP, Tokyo Ohka Kogyo Co., Ltd.) was spin-coated (1000 rpm for 5 s and 4000 rpm for 30 s), the substrates were baked at 338 K for 5 min. Photoresist (XP KMPR-1010, Kayaku Microchem) was spin-coated onto them (700 rpm for 5 s and 2900 rpm for 30 s). After baking (343 K for 5 min and 368 K for 10 min), UV (360 mJ/cm^2) was exposed on the samples through photomasks. The resulting samples were baked at 368 K for 6 min. To develop the samples, they were immersed into tetramethylammoniumhydroxide (TMAH) solution (2.38 wt %) for 8 min, and washed with ion-exchanged water.

Electrochemical Deposition. Electrodeposition of Ni was carried out using a Watts nickel bath ($NiSO_4 \cdot 6H_2O$, 240 g/L; $NiCl_2 \cdot 6H_2O$, 45 g/L; H_3BO_3, 35 g/L; sodium dodecyl sulfate, 0.15 g/L). The ITO plate patterned with photoresist and a Ni plate were immersed into the electrodeposition bath, and constant current (15 mA) was applied for 30 min. The obtained sample was washed with water and dried at room temperature.

Removal of Photoresist Layers. To remove photoresist layer, ITO plates electrodeposited with Ni were immersed into tetrahydrofuran for 10−20 min. A small amount of photoresist layer remained on ITO plates were removed by brushing.

Preparation of Nanomaterial Films. Single-walled carbon nanotubes (SWNTs, Wako Chemical Co. Ltd.) or TiO_2 nanoparticles (mean diameter =36 nm, C. I. Kasei Co., Ltd.) were added into ethanol to be 5 g/L of dispersions. After ultrasonic radiation, 0.3 mL of the dispersion was dropped on the substrates, and then dried at room temperature.

Removal of Ni Films. Ni thin films were removed by physical or electrochemical methods. In physical method, the rear side of the above sample was scratched by automatic linear precision saw, and split it up manually. The Ni thin films were carefully stripped off from the substrates. In electrochemical method, the sample was oxidized by applying constant current (15 mA) for 30 min in the electrodeposition baths.

Characterization. Scanning electron microscopy (SEM; VE-8800, Keyence) images were obtained at 5 kV. Energy dispersive X-ray spectroscopy (EDS) elemental mappings were carried out by using JED-2300 (JEOL) equipped with SEM (JSM-5310, JEOL). Optical micrograph images were measured by using an optical microscope (Digital Microscope VHX-200, Keyence).

RESULTS AND DISCUSSION

Photographs of stripping process of patterned Ni thin films are shown in Figure 1. To strip off Ni thin films from ITO plates, the sample was split from its rear side and Ni films were carefully peeled off. As expected, the patterned Ni thin films were smoothly stripped off from the ITO plates (Figure 1a). In addition, although the procedure was manually operated, the thin Ni films were not broken through the stripping process. The substrate after splitting off the Ni films was grayish and transparent (Figure 1b).

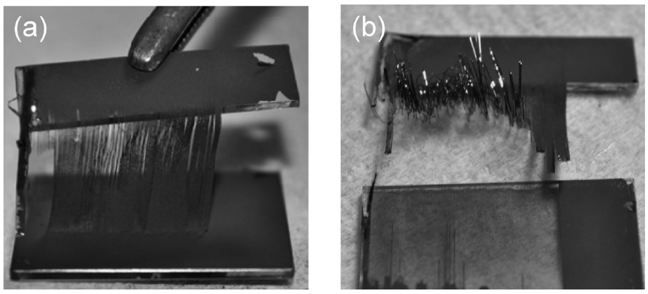

Figure 1. Photographs of stripping process of electrodeposited Ni thin films.

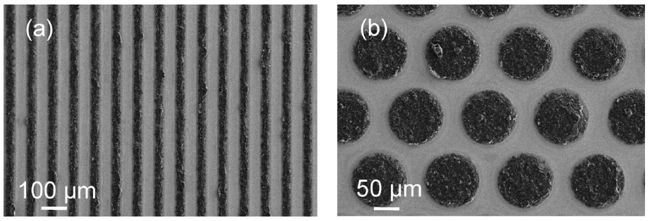

Figure 2. SEM images of (a) line-patterned and (b) circular-patterned SWNT thin films.

At first, we will show the fabrication of patterned SWNTs, as an example. A SEM image of the sample after stripping off Ni films was shown in Figure 2. We can see that line-patterned SWNTs with width of 40 μm were regularly formed (Figure 2a). SWNTs were not observed on the exposed area of ITO plates. In addition, this method could apply to prepare different shapes of patterned SWNTs thin films: photoresists were patterned in circular shapes on ITO plates, electrochemical deposition of Ni was carried out, photoresist layers were removed, SWNTs were casted over them, and then the Ni film was stripped off, in the same way. As a result, the electrodeposited Ni thin film was similarly removed, and circular-patterned SWNTs were remained on the substrates (Figure 2b).

Some researchers reported that CNTs could controllably assemble on substrates, based on chemically different natures of surfaces (e.g., two types of functional groups were patterned on substrates).[11,18,19] In our method, difference in chemical natures between Ni and photoresist had no influence on patterning SWNTs because we observed SWNTs deposited over both Ni areas and the exposed ITO areas in SEM images of samples before stripping off Ni films (not shown as figure), i.e., stripping procedure of Ni thin film is indispensable for patterning nanomaterials.

The Ni films can be removed by not only the stripping procedure but also electrochemical oxidation. Figure 3 shows optical micrograph images of SWNT layers on ITO substrates electrodeposited with Ni thin films (a) before and (b) after the electrochemical oxidation. In Figure 3, the boundary of SWNT films were shown. It is clear that the SWNTs were remained on the ITO plates after the electrochemical oxidation: the appearances of SWNT films were not

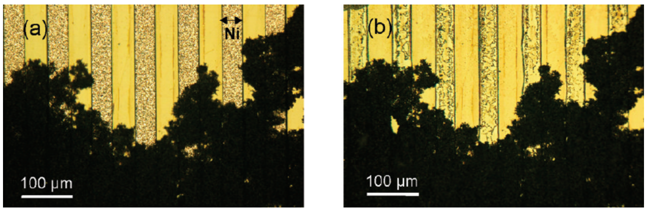

Figure 3. Optical micrograph images of SWNT layers on ITO substrates electrodeposited with Ni thin films (a) before and (b) after the electrochemical oxidation.

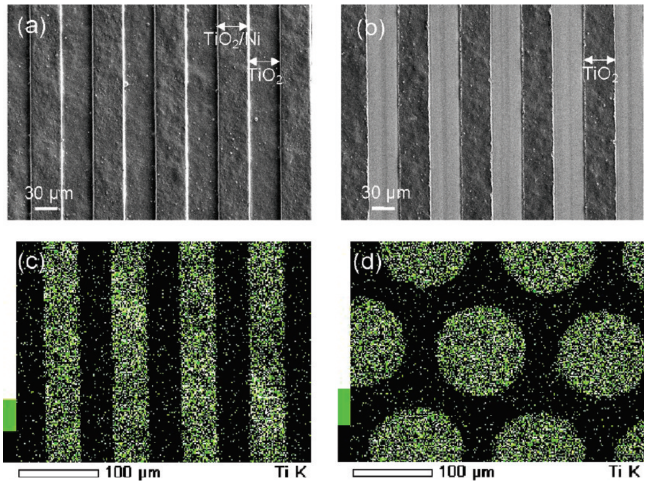

Figure 4. SEM images of (a) TiO_2 nanoparticles films on ITO substrates electrodeposited with Ni thin films and (b) patterned TiO_2 nanoparticles by the exfoliation of the Ni thin films. (c and d) Energy dispersive X-ray spectroscopy (EDS) elemental mappings of the patterned TiO_2 nanoparticles films.

changed. In the electrochemical oxidation, Ni metal is dissolved into solution as Ni^{2+} ions ($Ni \rightarrow Ni^{2+} + 2e^-$), and the Ni^{2+} ions are small enough to move through void spaces of SWNT layers. During the dissolution process, the remained SWNTs would prefer to be on ITO plates rather than move toward solution. It could be concluded that the dissolution of Ni films could not be a driving force to pattern nanomaterials. On the other hand, in physical stripping of the Ni thin film, SWNTs on the Ni thin films are forcibly removed; therefore, the exfoliation of Ni films is effective for patterning nanomaterials. Bradley and deMello et al. propose interlayer lithography, in which materials (e.g., SWNTs) deposited onto photoresist films were immersed in a developer and subjected to mild ultrasonic agitation to remove the soluble parts of the photoresist layer together with the overlying materials, leaving a thin patterned film of the target materials over a likewise patterned film of the photoresist.[20,21] In their study, the photoresist layer which is dissolved by a developer is the interlayer to prepare patterned films. On the other hand, the strippable Ni thin layer is the interlayer in our study. When photoresist layer is used as the interlayer, nanomaterials are patterned onto the remained photoresist layers. In the case of strippable Ni films, nanomaterials are directly deposited on the substrates. Thus, there is difference in the resulting patterned films because of differences in the type of the interlayers.

Since chemical and physical natures of nanomaterial have no influence in the preparation of patterned films, the method can apply to not only SWNTs but also various nanomaterials. As an example, patterned TiO_2 nanoparticles were prepared. Figure 4a and 4b show SEM images of TiO_2 nanoparticle films before and after stripping off Ni thin films. In the SEM image of the sample before stripping off Ni thin films, it seems that TiO_2/Ni layer is higher than TiO_2 layers, which indicates the presence of Ni films with height in micrometer-scale. After stripping off the Ni films, line patterns of TiO_2 nanoparticles were observed. In the EDS mapping of the sample after stripping off Ni films showed that TiO_2 nanoparticles were clearly distributed in linear or circular shapes. In addition, signals for Ni atoms were not observed in Figure 3c and 3d. The results suggested that patterned Ni thin films were completely stripped off by the simple and manual procedure, and only TiO_2 nanoparticles on the Ni strips were removed.

In addition to the simplicity, an attractive feature of the method is its mild preparation conditions, especially in the processes d and e shown in Scheme 1. It is well-known that nanomaterials are unstable due to their high surface energy; therefore, they tend to sinter to increase their sizes, which leads to the loss of the unique properties seen in the original nanomaterials.[22−24] Moreover, chemical treatments often change the surface property of CNTs or nanoparticles.[25−27] In our method, dropping nanomaterial dispersion and stripping off Ni films are operated at room temperature and atmospheric pressure without any chemical treatments, which indicates that nanomaterials are not damaged through the processes. This is an attractive feature in patterning of a variety of nanomaterials.

CONCLUSIONS

A novel and general patterning method using electrodeposited Ni thin films as a strippable mask was developed. ITO plates were patterned with an insulating photoresist by conventional photolithography, and Ni was electrodeposited on only the exposed ITO areas. After removing the photoresist layers, the substrates were evenly covered with nanomaterials such as SWNTs and TiO_2 nanoparticles by a drop cast method. The patterned Ni thin films deposited on ITO plates were manually stripped off and nanomaterials on the Ni film were simultaneously removed, leading to the formation of patterned nanomaterial films. This is the first report that electrodeposited metal films can be utilized as a strippable mask in material design fields. The method can apply to various nanomaterials such as nanotubes and nanoparticles because chemical and physical natures of nanomaterials do not have any influence to prepare patterned films. In addition, all the procedures are carried out at mild temperatures and atmospheric pressure, and sophisticated instrumentation, specialized reagents and/or severe preparation conditions are not required.

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