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Full Length Article

Rapid localized deactivation of self-assembled monolayers by propagation-controlled laser-induced plasma and its application to self-patterning of electronics and biosensors

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ABSTRACT

We present a novel laser-induced surface treatment process to rapidly control the spatial wettabilities of various functional solutions with submicron to micron resolutions. Ultrathin hydrophobic self-assembled monolayers (SAMs) that little absorb typical laser lights due to short penetration depth were selectively deactivated by instantaneous interaction with laser-induced metallic plasmas. The spatial region of the deactivated SAM, which corresponds to process resolution, is adjustable by controlling the spatial propagation of the plasma. This method leads to the parallel formation of hydrophilic functional solutions on glass substrates with a minimum resolution on the submicron scale. To show its feasibility in device engineering fields, this method was applied to the cost-effective fabrication of electronics and biosensors. Rapid self-patterning of electronic and biological functional solutions (silver nanoparticle solution and streptavidin protein solution) was successfully realized by selective deactivation of two different SAMs (tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) for electronics and the hetero-hybrid SAM (octadecyltrichlorosilane (OTS)/2-[methoxy(polyethyleneoxy)propyl] trichlorosilane (PEG)) for biosensors). As a result, this method can be exploited for the rapid and low-cost fabrication of various thin film devices such as electronics, biosensors, energy, displays, and photonics.

1. Introduction

Patterning of functional materials is widely used in the electronics, optical, biosensor, and multidisciplinary fields. Photolithography, which is the most representative method in micro-and nano-devices, has many merits such as high resolution, productivity, and a well-established mechanism [1–3]. However, non-preferable factors such as the need for toxic etchants, tight vacuum processes, expensive and complicated steps, and resistance to design change should be considered for successive patterning. To respond to recent consumer demands for thin, large-area, and low-cost devices, the fabrication method should be replaced with a more efficient and flexible manner. Solution-based processes such as ink-jet and roll-printing can satisfy the above requirements because they do not require photomasks, vacuum environments to deposit materials, and toxic and corrosive etchant; in addition, they enable direct fabrication of micropatterns without the need for photoresists and additional steps [4–7]. However, the resolution achieved by ink-jet printing is limited due to the nonlinear behavior of droplets, difficulty in controlling and fabrication of fine nozzles, and the time-consuming drawing procedure required in every process [8,9]. Process flexibility for easy design change is limited because an expansive template with micro-shape is required for roll-printing [10–12]. Therefore, a novel multiscale patterning regime enabling self-selective deposition of functional solutions including nanomaterials, biomaterials, etc. without the need for expensive pre-prepared templates is required to maximize flexibility and efficiency for the fabrication of a wide variety of microdevices. This is also a critical issue in bioengineering.

Self-assembled monolayers (SAMs) can be used as functional layers to change the surface energies of various substrates. Thus, they have been widely applied in the fabrication of various devices such as anti-stiction coatings, solar cells, and biological devices [13–16]. Because the long tail-like polymer chains at the end of the layer prevent polar solutions from being wetted, the layer was used as a representative hydrophobic layer [16,17]. The polar solutions with high surface tension are self-formed with a specific

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contact angle and are movable on the SAM without spreading on the non-SAM-treated region [16,18–20]. Self-patterning of polar solution can be realized by selectively creating the SAM with the width required for patterning resolution. Previous SAM patterning methods are divided into the deposition and etching regimes. The deposition methods such as contact printing and stamping need physical templates with complicated micro-features to selectively transfer the pre-formed SAM to the substrate [18,21,22]. The templates are expensive and not amenable to easy design change. Even if the etching methods have advantages in terms of simple and flexible fabrication compared to the deposition method, expensive facilities such as plasma and additional shadow masks are required to selectively defunctionalize the SAM [23–25]. The use of a shadow mask limits the achievable minimum resolution to several tens of micrometers and hinders the flexibility of the process. Irradiating a laser light could be the most effective method to fabricate SAM patterns, but it is impossible to remove or decompose SAMs on transparent substrates, such as glass, because the laser energy is not absorbed in the SAM due to its ultra-thinness that is typically less than 10 nm [21,26]. Although deep ultraviolet lasers can be used for the selective deactivation of functional layers through the direct photochemical dissociation of SAMs, the expensive light source and tight vacuum facilities are required [21,27–29]. In addition, ultrashort pulse lasers were also applied to deactivate SAMs with submicron resolutions via plasma filaments effect in air. However, the photon cost and process instability rise sharply due to the low stability of a light source and the range of achievable resolution is limited below 100 nm [30]. Therefore, a low-cost and high-resolution SAM patterning method based on a laser irradiation is required to realize the practical self-patterning of functional solutions.

In this paper, we report a novel rapid and digitalized SAM patterning process using the instantaneous decomposition interaction of SAM by propagation control of the laser-induced metallic plasma, as shown in Fig. 1(a). To show its feasibility for the self-patterning of functional materials for the wide application fields such as electronics and biosensors, silver-based microelectronics and the protein biosensor were directly fabricated by applying silver nanoparticle solution to the tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS)-patterned glass slide and protein solution to hetero-hybrid SAM (octadecyltrichlorosilane (OTS)/2-[methoxy(polyethyleneoxy)propyl]trichlorosilane(PEG))-patterned glass slide, respectively, as shown in Fig. 1(b) and (c).

2. Experiment section

2.1. Preparation of SAMs on glass slide

Two types of silane SAMs were employed depending on the target material of self-pattering and its application. Tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS, $CF_3(CF_3)_5(CH_2)_2SiCl_3$, Gelest, Aldrich 97%) was used as SAM material for self-patterning for electronics. To self-pattern for biosensor, a hetero-hybrid SAM obtained by mixing octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$, Gelest, Aldrich 90%) and 2-[methoxy(polyethyleneoxy)propyl]trichlorosilane (PEG, Gelest, $CH_3O(C_2H_4O)_{6\text{-}9}(CH_2)_3SiCl_3$) was employed to control the wettability of the target protein used in this study. Prior to depositing the SAMs, the glass slides were cleaned by immersion in a mixture of hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) in the ratio 1:3 and rinsing in distilled water. FOTS diluted in anhydrous toluene was uniformly deposited on the glass slide in a vacuum of 1 atm. The hetero-hybrid SAM with mixing ratio of 1:1 was also deposited on the glass slide using the same experimental procedure. To make the hetero-hybrid SAM (OTS/PEG), the cleaned slide glass was immersed in an anhydrous toluene chamber with 2 mM OTS and PEG organosilane solution for 30 min. It was post-cleaned via sonication in toluene for 10 min and by spreading acetone, methanol, and DI water. The mixing ratio of OTS and PEG was tuned within the mole fraction range 4:1–1:4.

2.2. Preparation for laser-induced metallic plasma

Chromium (used as an intermediate to generate laser-induced plasma) was deposited on a counter glass slide with a thickness of 100 nm using an electron beam evaporator. Ytterbium-doped pulsed fiber laser of 1070 nm wavelength and 200 ns pulse width (YLP-20, IPG Photonics Gmbh.) was employed as a light source to generate metallic plasma by interacting with the thin Cr layer. Spot sizes of 10 and 25 μm were obtained by integrating the laser with a 2D galvanometer and f-theta lenses of a focal length of 63 mm and 256 mm, respectively. The SAM-coated glass slide was placed opposite the Cr-coated slide with a gap of several microns. The relative separation distance and tilting (pitch and roll) of the SAM-coated glass with respect to the Cr-coated glass were precisely adjusted using a three-axis mounting system, as shown in Fig. S1. The mounting procedure is not complicated and time-consuming because the compensation of two tilting angles is required for initial setup. The laser was irradiated onto the Cr-coated glass through the SAM-coated glass. The pulse energy, pulse repetition rate, and scan rate were adjusted to determine the proper SAM removal region.

2.3. Self-patterning of silver electrode

A silver nanoparticle (Ag NPs) solution (NINK) was provided by ABC Nanotech Co. Ag NPs with average size of 20 nm were dispersed in a propylene glycol monomethyl ether (PGME), as shown in Fig. 2(a). The weight ratio and viscosity of the resultant Ag NP were 30% and 5.7 cp, respectively. Because its mobility on the SAM was similar to that in water, the solution deposited on the SAM was smoothly removed from the glass without drop formation. After immersing the Ag NP solution, the glass slide was baked in an oven hotter than 250 °C for 10 min. The self-patterned Ag electrode was characterized by optical microscopy, scanning electron microscopy, and using a probe station.

2.4. Self-patterning of biosensor

The laser-processed SAM specimen was immersed in ethanol solution containing 1% (v/v) 3-aminopropyltrimethoxysilane (APTMS, Aldrich, $H_2N(CH_2)_3\text{-}Si(OCH_3)_3$) for 4 h to graft a monolayer of APTMS on the plasma-treated regions. It was cleaned via ultra-sonication in ethanol for 10 min, washing with DI water, and drying by N_2 gas injection. To hold cyanine (Cy) 3-labeled streptavidin on the laser-processed region, chemical interaction between biotin and streptavidin are required; thus, the substrate was placed in *N*-Hydroxysuccimido (NHS)-biotin of 50 mM in dimethyl sulfoxide (DMSO, Aldrich, $(CH_3)_2SO$) at 25 °C for 30 min and washed with phosphate-buffered saline (PBS) and DI water. Biotin was selectively formed only on the ATMS region owing to the NHS reaction with the NH_2-terminated functional group. Streptavidin Cy3-labeled solution (10 g/mL) was applied along the edge of a glass bar; the bar was then carefully wiped in parallel under a gap of 100 μm and a constant velocity of 2 mm/s, as shown in Fig. 1(c). The specimen was incubated at 25 °C for 30 min in a moisture chamber to avoid evaporation of the streptavidin solution. To remove the solution from the non-laser irradiated region, the specimen was washed with PBS containing 0.01% (v/v) Tween 20 (PBS-T), PBS buffer, and DI water.