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Calcination-free micropatterning of rare-earth-ion-doped nanoparticle films on wettability-patterned surfaces of plastic sheets

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ABSTRACT

We demonstrate a patterning technique of rare-earth-ion-doped (RE) nanoparticle films directly on wettability-patterned surfaces fabricated on plastic sheets in one step. Self-assembled monolayers consisting of silane-coupling agent with hydrophobic groups were fabricated on plastic sheets. UV–ozone treatments were performed through a metal mask to selectively remove the self-assembled monolayers in a patterned manner, resulting in the formation of wettability-patterned surfaces on plastic sheets. Using a water dispersion of Er^{3+} and Yb^{3+}-codoped Y_2O_3 nanoparticles at a diameter of 100 nm, RE-nanoparticle films were fabricated on the wettability-patterned surfaces by a dip-coating technique. By adjusting the concentration of RE-nanoparticle dispersion, withdrawal speed, and withdrawal angle, amount of RE-nanoparticles, we were able to control the structures of the RE-nanoparticle films. Fluorescence microscope observations demonstrate that visible upconversion luminescence and near-infrared fluorescence were emitted from the RE-nanoparticle films on the wettability-patterned surfaces. This technique allows for the fabrication of flexible emitting devices with long-operating life time with minimized material consumption and few fabrication steps, and for the application to sensors, emitting devices, and displays in electronics, photonics, and bionics in the future.

1. Introduction

Two-photon absorption materials which can convert near-infrared light to visible light have attracted much attention for the fabrication of three dimensional transparent displays [1–4]. Upconversion luminescent intensity is proportional to the square of excited light intensity, leading to high resolution imaging on the displays. Two-photon absorption materials consisting of inorganic ceramics are suitable for the fabrication of displays because of the necessity of the exposure of the displays to excited light at high power for a long time [2,4]. Patterning techniques for waveguide and emitting layers are required to fabricate thin transparent displays operating without condenser lens for focusing excited light or laser scanners [5,6].

Rare-earth-ion-doped (RE) ceramics have widely been studied for the applications to light emitting devices emitting at three wavelengths [7–9], sensitizers in solar cells [10–12], bio-imaging materials [13,14] as well as displays. Photolithography has been utilized for the patterning of RE phosphor films fabricated on solid substrates by electrophoresis [15], screen printing [16], and sol–gel [17] techniques. Soft lithography has been reported for the direct fabrication of RE phosphor films using elastic stamps [18–21]. This technique enables the direct fabrication of patterned RE phosphor films without etching or liftoff, leading to reduced material consumption and fabrication steps compared with conventional photolithography. Recently, RE nanoparticles allow for the fabrication of RE phosphor films at the nanometer length scale by soft lithography and techniques utilizing self-assembling processes [22–24]. However, these techniques require calcination processes after the formation of RE precursor films, rendering the fabrication of RE phosphor films on plastic sheets difficult.

We have reported calcination-free fabrication techniques for the patterning of RE phosphor films on plastic sheets by using RE nanoparticles as film-forming materials. RE nanoparticle films were fabricated on the whole area of patterned photoresist films on plastic sheets followed by rinsing with acetone for liftoff, resulting in the formation of patterned RE nanoparticle films on plastic sheets [25,26]. Recently, we reported a new calcination-free technique for the direct patterning of RE nanoparticle films by micromolding in capillary which is one of the soft lithography techniques [27]. The photolithographic techniques have potential problems in fabrication cost due to material consumption of photoresist and RE

Abbreviations: RE, rare-earth-ion-doped; HMDS, hexamethyldisilazane; F8H2SiOEt, heptadecafluoro-1,1,2,2-tetrahydrodecyltriethoxysilane; ITO, indium–tin–oxide; PEN, polyethylene naphthalate.

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nanoparticles after the liftoff process. In the case of micromolding in capillary, the shape of the patterned RE phosphor films is limited in line/space and holes. Wettability-patterned surfaces which consist of the hydrophilic surface of the substrates surrounded by the hydrophobic surface of self-assembled monolayers will find applications to the direct photoresist- and stamp-free fabrication of RE nanoparticle films on substrates. These surfaces enable the patterning of functional material films through both dry and wet processes in one step because molecules or their solutions are selectively deposited on the high or low surface free energy regions on the substrates. We have reported the direct fabrication of fluorescent dye films, J-aggregates dye films and metal films on wettability-patterned surfaces fabricated from mixed phase-separated Langmuir–Blodgett films on Si wafers [28–30].

In this study, we aim at the direct fabrication of RE nanoparticle films on wettability-patterned surfaces of plastic sheets without photoresists or stamps. RE nanoparticles were synthesized according to the literature [8,25] and were dispersed in water. Wettability-patterned surfaces were fabricated by formation of self-assembled monolayers consisting of silane-coupling agents having hydrophobic groups on glass and plastic sheets. RE-nanoparticle films were fabricated by dip-coating with variations in fabrication conditions. Samples were characterized mainly by optical, fluorescence and scanning electron microscopies. This technique will allow for the flexible RE phosphor films without using photoresists or stamps, leading to the reduction of material consumption and fabrication steps.

2. Experiment

2.1. Materials

Er^{3+}- and Yb^{3+}-doped Y_2O_3 nanoparticles were synthesized according to the literature [8,25]. $Y(NO_3)_3{\cdot}6H_2O$, $Er(NO_3)_3{\cdot}5H_2O$, $Yb(NO_3){\cdot}5H_2O$, and urea were purchased from Aldrich. Acetone and chloroform used for cleaning substrates were obtained from Wako. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) and heptadecafluoro-1,1,2,2-tetrahydrodecyltriethoxysilane (F8H2SiOEt) used for formation of self-assembled monolayers on glass and plastic sheets, respectively were obtained from Aldrich and AZmax. Hexane used for dissolving F8H2SiOEt was purchased from Wako. Glass plates and indium-tin-oxide (ITO) deposited on polyethylene naphthalate (PEN) sheets were purchased from Matsunami Glass Ind., Ltd. and Oike Co., Ltd., respectively.

2.2. Patterning procedures of RE nanoparticle films

Glass plates and ITO/PEN sheets were ultrasonicated in acetone and chloroform for 20 min each, and were exposed to UV–ozone atmosphere for 15 min generated with a PL16-110 UV–ozone cleaner (Sen Lights Corp., Japan). The contact angle of water was less than 5° on the glass plates. Glass plates and ITO/PEN sheets were immersed in neat liquid of HMDS overnight and in a 2 mM hexane solution of F8H2SiOEt for 24 h, respectively. The substrates were rinsed with water and then heated at 110 °C for 30 min to form covalent bonds between the silane-coupling agents and the substrates. The contact angle of water was about 109° on the self-assembled monolayers of HMDS on the glass plates. The self-assembled monolayers were selectively removed by UV–ozone treatments through metal masks with patterns of line slits at a width of 100 μm and length of 4 mm or with patterns of holes at a diameter of 30 μm, resulting in the formation of wettability-patterned surfaces which consist of the hydrophilic surfaces of the substrates surrounded by the hydrophobic surfaces of the silane-coupling agents (Fig. 1a).

RE nanoparticle films were fabricated on the wettability-patterned surfaces using a dip-coating technique. RE nanoparticle dispersion was prepared by adding RE nanoparticles in water and then ultrasonicating for 1 h. The wettability-patterned templates were immersed in the RE nanoparticle dispersion and withdrawn at specific speeds and withdrawal angles θ with respect to the surface of the bottom of the vial containers under air blowing with a wind speed of about 3.5 m s^{-1} at a temperature of about 40 °C (Fig. 1b and c).

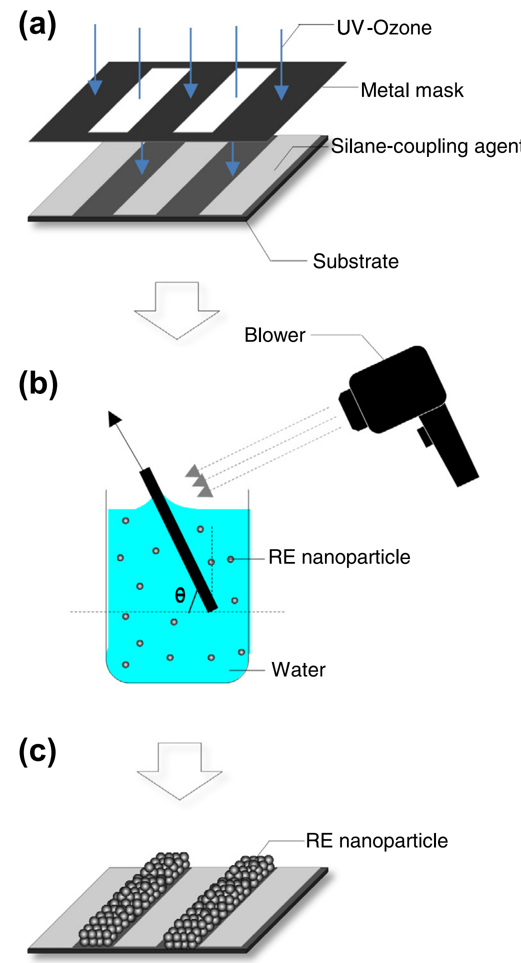

Fig. 1. Fabrication scheme: (a) fabrication of wettability-patterned surface, (b) dip-coating, and (c) formation of RE nanoparticle films on wettability-patterned surface.

2.3. Characterization

Optical microscope observations were performed with a BX-60 optical microscope (Olympus, Japan). Upconversion emission spectra in visible region were obtained on an RF-5000 visible spectrometer (Shimadzu, Japan), and near-infrared fluorescent spectra were measured on a near-infrared spectrometer (AvaSpec, USA) and a semiconductor laser diode operating at 980 nm. Visible upconversion luminescence and near-infrared fluorescence imaging was carried out with an IX-71 optical microscope (Olympus, Japan) equipped with a visible CCD camera (DP20, Olympus) and a near infrared CCD camera (XEVA-474, Xenics). The emission images were obtained through a band-pass filter at 550 or 650 nm and a short-pass filter at 900 nm. SEM observations were made with an S-4200 microscope (Hitachi, Japan).

3. Results and discussion

We investigated upconversion luminescence and fluorescence properties of the RE-nanoparticles.