Large-area In$_2$O$_3$ ordered pore arrays and their photoluminescence properties

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ABSTRACT Large-area In$_2$O$_3$ ordered pore arrays were prepared on glass and silicon substrates by the sol-gel technique based on colloidal monolayer spheres. The morphologies of such arrays are determined by precursor concentration used and colloidal sphere size, and are thus controllable. It has been shown that the formed ordered pore arrays consist of In$_2$O$_3$ polycrystallines. The photoluminescence measurement of the In$_2$O$_3$ ordered pore arrays shows that there is a strong photoluminescence band in the blue-green region centered around 465 nm, which does not exist in the bulk materials. Further experiments reveal that this peak originates from the oxygen deficiencies in In$_2$O$_3$ skeletons. This polydomain ordered pore-structured array could be of great potential for Si-based integrated nanophotonics and optoelectronic devices of the next generation, in addition to new gas sensors.

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1 Introduction

Indium oxide (In$_2$O$_3$) is a wide band gap transparent n-type semiconductor (direct band gap energy of 3.55–3.75 eV), which has been widely used in the microelectronic field as selective transparent coatings, selective gas sensing materials [1–3], and transparent electrodes [4, 5]. Recently, low-dimensional nanostructures of In$_2$O$_3$ with different morphologies have also been extensively reported, such as nanofibers [6], metal-filled nanotubes [7], ordered nanowire arrays [8, 9], nanoparticles dispersed within pores of mesoporous silica [10, 11], and size-controlled In$_2$O$_3$ nanoparticles [12]. The In$_2$O$_3$ films were prepared by various physical vapor deposition and chemical methods such as thermal evaporation, rf sputtering, dc sputtering, ion plating, oxygen ion assisted deposition, and sol–gel methods [13–18]. Ordered porous films have received considerable attention in recent years [19–23] due to their unique properties and potential applications in catalyses [19], photonic crystals [20], and optoelectronic devices [21]. They are also excellent substrates for surface-enhanced Raman spectroscopy (SERS) [23] and cell cultures [24]. However, to our knowledge, there has been no report on an In$_2$O$_3$ thin film with such ordered pore arrays. We report in this work a new route for the synthesis of In$_2$O$_3$ films structured with ordered pore arrays on glass and silicon substrates based on a colloidal monolayer template-directed sol dipping method. Their morphologies can be controlled by precursor concentration and size of colloidal spheres. Such an ordered pore array shows a blue-green luminescent peak around 465 nm, which could be of great potential to be Si-based integrated nanophotonics and opto-electronic devices of the next generation due to such an ordered structure, in addition to new gas sensors.

2 Experimental

Ordinary glass and silicon(100) substrates were ultrasonically cleaned in acetone and then in ethanol for one hour, as previously described [25–27]. Polystyrene sphere (PS) (1000 nm and 350 nm in diameter) suspensions (2.5 wt. % in water, surfactant-free) were from Alfa Aesar Company (standard deviation of the diameter of the PSs is less than 5%). The colloidal sphere monolayer with a large area (> 1 cm$^2$) was prepared on the cleaned glass substrate by spin coating on a custom-built spin coater. The monolayer is formed based on a capillary force-induced self-assembly process of PSs on the substrate with a smooth and hydrophilic surface. The experimental details can be found elsewhere [28]. A 1000-nm PS suspension of 10 µl in volume was spin coated at low speed (~100 rev/min), while spin coating of 350-nm PSs of 4.0 µl was performed at a higher speed (~850 rev/min). Some of them were transferred on to a Si substrate by lifting off in water and picking up with the silicon wafer, as illustrated in Fig. 8 of [27].

The precursor sols used in this work were prepared as follows: NH$_3$·H$_2$O solution was added to the 0.5 M InCl$_3$ solution slowly until In(OH)$_3$ precipitated completely. The product was rinsed several times with millipore water until all Cl$^-$ ions were removed (tested with AgNO$_3$ solution). A certain amount of the powder was dispersed in 0.25 M nitric acid and its pH value was controlled at 2.4–2.5 by gradually adding NH$_3$·H$_2$O solution [18]. We thus obtained stable, homogenous, and translucent precursor sols with indium concentrations of 0.2, 0.35, and 0.5 M, which had an obvious Dindal effect when a beam of a laser (532 nm) passed through them.
In$_2$O$_3$ ordered pore arrays were fabricated as schematically illustrated in Fig. 1. A droplet of the preformed sol is first dropped on to the two-dimensional (2D) monolayer colloidal crystal with a quantitative pipette, which can infiltrate into the interstices between the substrate and the colloidal monolayer, followed by drying at 110 °C and ultrasonically washing in methylene chloride ($\text{CH}_2\text{Cl}_2$) for 2 min to remove the template (the PS spheres can be dissolved quickly in the CH$_2$Cl$_2$ solution). Finally, the sample is annealed in air at 400 °C for 1 h for the decomposition of In(OH)$_3$ into In$_2$O$_3$.

The synthesized products were characterized by X-ray diffraction (XRD, Philips X’Pert using Cu $K_\alpha$ line and $\lambda = 0.15419 \text{nm}$) and field emission scanning electron microscopy (FE-SEM, JEOL 6700) as well as transmission electron microscopy (TEM, JEM-200CX). Photoluminescence (PL) spectra were measured but only for the samples with silicon substrates because there exists a PL signal in glass substrates in the region studied, which will conceal that of the thin In$_2$O$_3$ film. The measurements were performed at room temperature on a FLS920 PL spectrophotometer with a Xe lamp and a 400-nm filter. An energy-dispersive spectrum of X-rays (EDX) was recorded on a Kevex Sigma™ gold energy dispersive X-ray analysis system.

3 Results and discussion

By a spin-coating method, a large-area colloidal monolayer (> 1 cm$^2$) was successfully fabricated, as typically shown in Fig. 2, which was taken in the edge region of the PS film on a glass substrate. We can see that the PSs have crystallized and formed a monolayer with the closely packed hexagonal lattice through a self-assembly process, which has been extensively studied [28–31].

Figure 3 shows the pore arrays on glass substrates after removal of the templates and annealing at 400 °C for the samples with different concentrations of the precursor sols. All exhibit a well-defined honeycomb shape from top view. With increase of precursor concentration from 0.2 M to 0.5 M for the samples with a template of 1000-nm PSs, the depth of the pores in the array increases from less than the radius of the PSs (Fig. 3a) to larger than that of the PSs (Fig. 3c). But, there is no obvious change of the pore size on the film surface (from top view) with the concentration, since the pore depth is around the radius value at which the pore size at the surface from top view is insensitive to the depth, as schematically illustrated in Fig. 4. Nevertheless, for the samples by templates with much smaller PSs (350 nm), the pore size at the film surface evolves with the concentration significantly, as indicated in Fig. 3d and e. The higher concentration leads to the deeper pores. In Fig. 3e, the deeper pores can be seen clearly, and they seem to be hollow spheres with cut-off tops. The reason for the formation of pores with different depths is easily to be understood since higher-concentration precursors contain more solute per unit volume. For the samples with Si substrates, the morphologies are similar to those of the corresponding samples on glass substrates shown in Fig. 3. The morphologies of the ordered pore arrays are determined by precursor concentration and PS size, which are controllable. Figure 5 shows the XRD results for the ordered pore arrays before and after annealing. Before annealing (after removal of the monolayer), the skeleton is composed of In(OH)$_3$, as shown in Fig. 5a, which is not well crystallized. After annealing at 400 °C in air, however, the skeleton has changed into In$_2$O$_3$ crystal with body-centered cubic structure (see Fig. 5b). Its lattice constant is 10.1 Å, which is consistent with the standard value for the bulk (JCPDS 71-2195). The final ordered pore array was re-