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Regular Article

Visible and near-infrared luminescent properties of Pr^{3+} doped strontium molybdate thin films by a facile polymer-assisted deposition process

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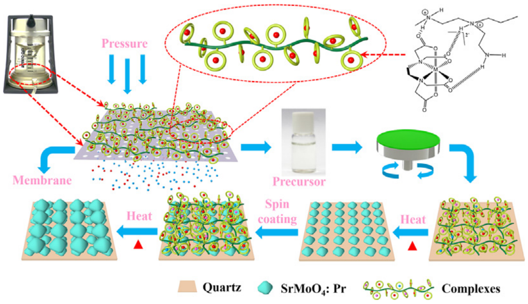
GRAPHICAL ABSTRACT



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ABSTRACT

Quartz substrate supported Praseodymium (Pr) doped strontium molybdate ($SrMoO_4$) thin films with good uniformity and outstanding fluorescent properties are successfully fabricated via a facile polymer-assisted deposition (PAD) method. In combination with the strong chelating effect of water-soluble polymer on metal cations, the free cations without chelating are effectively ruled out but the remaining chelating metal cations are employed for the highly uniform and accurate stoichiometry luminescent $SrMoO_4$: Pr thin films, layer-by-layer mounting on the common quartz substrates. More importantly, the excellent release of stress from polymer during the growth process of epitaxial thin film can effectively overcome the mismatch between thin film and common quartz substrate and then guarantee the quality of thin film. Under the ultraviolet (UV) light excitation, the samples show high luminescence intensity both in visible and near-infrared (NIR) regions peaked at 646 nm and 1037 nm, mainly ascribing to the transitions of $^3P_0 \rightarrow {}^3F_2$ and $^1G_4 \rightarrow {}^3H_4$ of Pr^{3+} ions. The luminescent properties can be tailored by optimizing the number of spin-coated layers and doping concentrations. The maximum emission occurs at 4 mol% of Pr^{3+} dopant, and it exhibits an impressive high photoluminescence quantum yield (QY) of up to 86.12%. These results evidently demonstrate the present PAD method is a useful prototype for preparing high performance luminescent thin films even on the cheap quartz substrate.

1. Introduction

Recently, metal molybdates ($RMoO_4$), emerged as promising host materials in phosphors industry, have received considerable

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research attentions due to their high thermal and chemical stability, high light yield, high average refractive index and versatile potential applications [1–3]. Generally, $RMoO_4$ (R = Ca, Ba, Sr, Pb) share the scheelite-type structure, and this kind of the unique crystal structure has been confirmed to possess more excellent optical performance than other crystal structures. As a promising alternative material used in white LEDs, every centrally located Mo atoms in molybdates ($RMoO_4$, R = Sr, Ba, Ca et al.,) is coordinated by four O atoms to form the stable structure MoO_4^{2-}, which will absorb the external energy in the near ultraviolet (UV) and then transfer energy to rare earth ions [4,5]. It has been reported that the $RMoO_4$ have been doped feasibly by rare-earth metals, such as Dy^{3+}, Tb^{3+}, Sm^{3+}, and Eu^{3+}, which showed enhanced luminescent properties with broad and intense absorption bands due to the charge transfer [4,6]. Among the various molybdates, $SrMoO_4$ possesses the unique advantages of low phonon energy, wide band gap, and stable structure, leading potential application in luminescence devices [7]. So, rare earth ions activated $SrMoO_4$ phosphors are extensively investigated, indicating complicated energy level scheme and diverse optimal emission in various host materials. Dunaeva et al. [8] and Cao et al. [9] applied the Czochralski technique to grow a Pr^{3+}-doped $SrMoO_4$ single crystal, and the heat conductivity and luminescence lifetime were improved by doping Pr^{3+} ions. In addition, Xia et al. used high-temperature solid-state reaction method to prepare Pr^{3+}, Yb^{3+} and Sm^{3+} co-doped $SrMoO_4$ phosphors [10]. These studies indicate an exciting phenomenon that a new near-infrared (NIR) emission around 1040 nm can be attributed to the $^1G_4 \rightarrow {}^3H_4$ transition of Pr^{3+} ions. NIR emission materials are closely relevant to widespread applications, such as bio-imaging, optical telecommunications, amplifiers, and waveguides [1,11–14]. However, the conventional fluorescent phosphors for white LEDs present the heat dissipation issues, and it is difficult to get the uniform white light. In contrast, the fluorescent thin films exhibit higher uniformity, better adhesion, higher resolution and superior thermal conductivity when they are applied in displays and sensors for stress and temperature, it is a desired form for the solid-state device [15,16]. Generally, the fluorescent thin films mostly synthesized via pulsed laser deposition, ion-beam evaporation, RF sputtering and laser ablation methods in which expensive equipment or complicated process are compulsory to hinder their further commercial applications [17–19]. Furthermore, the stronger interfacial stress caused by the mismatches between thin film and common substrate is still a great challenge to date. Hence, it is essential to seek for simple and convenient means to prepare high-quality fluorescent thin films. In our previous work, broccoli-like superparticles were prepared by a polymer-assisted hydrothermal method [20]. The metal ions bind to the water-soluble polymers to effectively control the nucleation and growth process, this render us some enlightenment to synthesize $SrMoO_4$: Pr^{3+} luminescent thin films.

Polymer-assisted deposition (PAD), firstly reported in 2004, acting as an aqueous chemical solution route is a simple and low-cost method for preparing high-quality metal epitaxial films such as single element materials, metal-oxides, metal-nitrides and metal-carbides [21–26]. PAD is proposed as an efficient method based on the chemical solution deposition, metal precursors and water-soluble polymer are main components, and the soluble polymer is used for binding with metal ions directly to control the nucleation and growth of highly crystalline epitaxial films [24,27]. The metal ions bonded by polymer can homogeneously distribute in the precursor polymeric solution, strongly prevent from attending in secondary chemical reaction and effectively control the growth stress of thin film mounted on the substrate [28]. Therefore, all above characteristics in PAD method are beneficial to prepare luminescent thin films with high quality. Furthermore, Pr^{3+}-doped $SrMoO_4$ thin films have never been investigated, and all the more so for the NIR luminescent emission of Pr^{3+} with various doping concentration.

In this paper, Pr^{3+}-doped $SrMoO_4$ multilayer luminescent thin films with good uniformity and high luminescent properties are successfully prepared on the common quartz substrate via the PAD method for the first time. The samples show high luminescence properties both in visible and NIR regions peaked at 646 nm and 1037 nm by the UV light excitation, and the thin films show exciting high photoluminescence quantum yield. These promising results obtained strongly suggest that the PAD method is a lighthouse for preparing high-performance luminescent thin films, even on low-cost common quartz substrate.

2. Experimental section

2.1. Preparation of precursor solution

In this present work, the raw materials were EDTA (Aldrich), PEI (99.99%, Aladdin), $Sr(NO_3)_2$ (AR, Keshi), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AR, Keshi), and $PrCl_3\cdot 6H_2O$ (99.99%, Aladdin). First, 1 g EDTA and 1 g PEI were dissolved in 40 mL deionized water. After that, $Sr(NO_3)_2$ were added to the former solution bit by bit with continuous stirring for 1 h at the room temperature. Then Amicon filtration was used at least 3 times to filtrate the solution, the filtrated solution was labeled as A. The solutions contain Mo^{2+} and Pr^{3+} are prepared with the same method, and these two solutions were labeled as B and C, respectively. The ultimate concentration of Sr^{2+}, Mo^{6+} and Pr^{3+} in the A, B and C solutions can be confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The actual concentration of Sr^{2+}, Mo^{6+} and Pr^{3+} ions are 7.46 mg/mL, 15.7 mg/mL and 13.55 mg/mL, respectively. Finally, the precursor solutions of $SrMoO_4$: Pr_c (c = 0.01–0.06) were obtained by mixing the filtrated solution of Sr^{2+}, Mo^{6+}, and Pr^{3+} ions with a desired molar ratio.

2.2. The growth of $SrMoO_4$: Pr thin films

Quartz substrates were cleaned several times with acetone and ethanol prior to deposition. The as-prepared precursor solution was spin-coated on quartz substrates at 600 rpm for 10 s and 3000 rpm for 20 s. Soft-baking on a hot plate at 100 °C in air for 10 min was required to remove the residual water. Finally, the precursor thin film was thermal treated in a muffle furnace. It was heated to 510 °C with a low ramp rate of 1 °C/min and dwelled for 2 h to make sure the thermal decomposition of PEI and EDTA. Then the samples were heated at a high ramp rate of 10 °C/min from 500 °C to 800 °C, after annealing for 30 min, the thin films were cooled down to 200 °C with the speed of 2 °C/min. The spin-coating and thermal treatment processes were repeated multiple times depending on the designed film thickness. Finally, high-quality luminescent thin films were obtained when the films were cooled down to the room temperature.

2.3. Characterization

The crystal structure and phase composition of Pr^{3+}-doped $SrMoO_4$ thin films were identified by the X′Pert Pro (Holland) X-ray diffract meter with Cu $K_{\alpha 1}$ radiation (λ = 0.15406 nm). SEM images of samples were examined using scanning electron microscopy (SEM, S4800). The photoluminescence and photoluminescence excitation spectra were investigated at room temperature using FLS980 (Edinburgh Instruments) spectrometer with a 450 W Xenon lamp. Their photoluminescence quantum yields were analyzed using the absolute photoluminescence quantum yield measurement system that came with FLS980 (Edinburgh