1. Introduction

Compared with phosphors crystals and powders, the rare-earth-doped luminescent thin films possess merits of higher contrast and resolution, superior thermal conductivity, greater uniformity as well as better adhesion to the solid substrate, attracting great interest in optoelectronic devices, ranging from bio imaging, drug delivery, solid state lasers, flat panel displays, integrated optics systems and many others [1–6]. Among these, the rare-earth elements doped scheelite tetragonal structured molybdate thin films have been increasingly important since the compelling of outstanding physicochemical stability and excellent photoelectric properties [7–11]. Especially, europium (Eu) doped BaMoO$_4$ various luminescent materials have received considerable attention due to its characteristic red emission of Eu$^{3+}$ at around 615 nm with potential applications in warm white light-emitting diodes (LEDs), lasers, display devices, to name a few [12–16].

Nevertheless, the current approaches to fabricate the luminescent films including pulsed laser deposition, sputtering, molecular beam epitaxy, chemical vapor deposition and spray pyrolysis generally suffer from the low luminescence efficiency, complicated manufacturing process and inaccurate regulation for the concentration of the rare-earth ions, which largely overshadows their further adoption in industrial-scale [17–19]. It is urgently needed to develop a feasible, low-cost, and controllable method to prepare high-performance luminescent thin films. In our previously reported works, the PAD method has been proved as a simple and low-cost pathway to generate luminescent thin films on the various substrates which can precisely regular the concentration of doping ions [6,8]. However, the emission intensity of the luminescent thin films fabricated by PAD is relatively low for practical application owing to their large lattice mismatch with the substrate, indicating that the interface controllability is still a big challenge.

Herein, we propose a grain orientation engineering strategy to remedy the defects caused by lattice mismatch, meanwhile, highly oriented BaMoO$_4$: Eu$^{3+}$ thin films are fabricated with significant enhancement of the luminescence properties. The monocrystal silicon (Si) is picked as substrates owing to its low cost and superior lattice compatibility, on which the BaMoO$_4$: Eu$^{3+}$ thin films are mounted [20–22]. To justify three effect of the orientation on the luminescence performance, three different oriented Si substrates are exploited to mount BaMoO$_4$: Eu$^{3+}$ thin films. The BaMoO$_4$: Eu$^{3+}$ thin films mounted on (111)-oriented Si substrates exhibit randomly orientation, while the BaMoO$_4$: Eu$^{3+}$ thin films mounted on (100)-oriented and (001)-
oriented Si substrates exhibit <112>-preferred and <004>-preferred orientation, respectively. The luminescence intensity of high-quality <004>-textured BaMoO₄:Eu³⁺ thin films can be improved 366% compared with the nontextured one. Furthermore, the luminescence performance of BaMoO₄:Eu³⁺ thin films can be further enhanced via tuning the annealing temperature, layers of thin film and concentration of Eu³⁺ ions. The BaMoO₄:Eu³⁺ thin films exhibit bright red emission at 615 nm corresponding to the ⁵D₀→⁷F₂ transition of dopant Eu³⁺ ions, uniform morphology, ultra-high color purity of nearly 100%, and correlated color temperature (CCT) of 2922 °C. Therefore, this demonstrated grain orientation engineering could open a door for the low-cost and high luminescence intensity thin films, which accelerates the progress of practical applications and industrialization.

2. Experimental section

2.1. Preparation of precursor solution

EDTA (99.99%, Aldrich), PEI (99.99%, Aladdin), Ba(NO₃)₂ (AR, Keshi), (NH₄)₆Mo₇O₂₄·4H₂O (AR, Keshi), and EuCl₃·6H₂O (99.99%, Aladdin) were used as the starting materials, and all the starting materials were used without further purification. 1g EDTA and 1g PEI were completely dissolved in 40 mL deionized water, then 1g Ba(NO₃)₂ were added slowly and stirred well to form a homogeneous solution. The solution was transferred into an Amicon filtration of 50 ml capacity, and it was filtrated at least 3 times under the pressure of N₂. The actual concentration of Ba²⁺ ions in the precursor solution was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the concentration is 20.22 mg/mL. Similarly, the solution of Mo⁶⁺ and Eu³⁺ was obtained by the above experiment approach and the actual concentration of Mo⁶⁺ and Eu³⁺ is 15.58 mg/mL and 13.52 mg/mL, respectively. Finally, the solution of Ba²⁺, Mo⁶⁺ and Eu³⁺ were mixed at the desired molar ratio of 1:1:x (x = 0.01-0.06) to obtain the precursor solution of BaMoO₄:Eu³⁺

2.2. The growth of BaMoO₄:Eu³⁺ thin films on different oriented Si substrates

The BaMoO₄:Eu³⁺ thin films were mounted on monocrystalline Si substrates with different orientations by the PAD method, the substrates including (111)-oriented, (100)-oriented and (001)-oriented Si. Prior to deposition, comprehensive cleaning of substrates was carried out by using acetone, ethanol, and deionized water. The precursor solution of BaMoO₄:Eu³⁺ was spin-coated on clean substrates at 1000 rpm for 10 s and 3000 rpm for 20 s, then baked on a heating stage at 100 °C to remove the residual water. After that, these samples were thermally treated according to the self-designed procedure in a muffle furnace as design. The processes of spin coating and thermal treatment were repeated several times depending on the need for thin-film thickness.
2.3. Characterization

The crystal structure and orientation of BaMoO₄: Eu³⁺ thin films were analyzed by the X'Pert Pro (Holland) X-ray diffract meter with Cu Kα₁ radiation (λ = 0.15406 nm) for 20 values in the range of 10–60°. The morphology and grain size distribution of BaMoO₄: Eu³⁺ thin films were identified by the FEI QUANTA EFG 250 scanning electron microscopy (SEM, S4800). The PL emission and excitation spectra of samples were measured using the FLS980 (Edinburgh Instruments) spectrometer with a 450 W Xenon lamp. The decay curves were recorded by the FLS980 spectrometer with a 60 W μs pulsed Xenon flash lamp at room temperature.

3. Result and discussion

The three-dimensional unit cell structure schematic representations of BaMoO₄ is presented in Fig. 1a, the structure was modeled according to the ICSD #50821. The structural of BaMoO₄ belong to the scheelite structure (tetragonal. I4₁/a (No. 88)), and the lattice parameters are a = b = 5.5479 Å, c = 12.745 Å, V = 392.22 Å and Z = 4 [15,16]. The Ba atoms are bonded to eight oxygens to form the polyhedral [BaO₈] of 7 atoms occupy the 4b sites, Mo atoms occupy the 4a sites, and O atoms Eu³⁺.

Fig. 2a. The emission spectra can be attributed to 5 clusters, and Mo atoms are coordinated to four oxygens to form the tetrahedral [MoO₄] clusters [23]. In the unit cell (Z = 4) of BaMoO₄, Ba atoms occupy the 4b sites, Mo atoms occupy the 4a sites, and O atoms occupy the 16f sites. The crystal structures of surfaces (112) and (001) are presented in Fig. 1b and c. Due to the ionic radius of Eu³⁺ (1.07 Å) is smaller than the Ba²⁺ (1.42 Å) ionic radius, Eu³⁺ ions are more likely to occupy the site of Ba²⁺ ions [16]. The XRD patterns of BaMoO₄: Eu³⁺ thin films mounted on the different substrate are illustrated in Fig. 1e, g and i. The diffraction peaks of these three samples are in good agreement with XRD reference data (JCPDS No. 08-0455) of BaMoO₄, there are no additional peaks were found [24]. The phase purity of samples indicates that Eu³⁺ ions were successfully incorporated into the BaMoO₄ host lattice as activators. The grain orientation of BaMoO₄: Eu³⁺ thin films can be controlled by using various-oriented Si substrates. Schematic of the crystal structure of non textured and textured BaMoO₄: Eu³⁺ thin films were illustrated in Fig. 1d, f and h. The nontextured BaMoO₄: Eu³⁺ thin film mounted on the (111)-oriented Si substrate shows two major orientations of (112) and (004), as shown in Fig. 1d and e. The high-quality textured samples can be fabricated using Si substrate with (100) orientation and (001) orientation. As shown in Fig. 1f and g, the < 112 >-textured sample shows an obvious enhancement in the intensity of (112) diffraction peaks, the Lotgering factor F₁₁₂ of the sample is 93.7% [25]. The < 004 >-textured sample shows a significant enhancement in the intensity of (004) diffraction peak, and the sample's Lotgering factor F₀₀₄ is as high as 94.6%, as illustrated in Fig. 1h and i. The ultra-high Lotgering factor reveals the strong (004)-preferred orientation of the BaMoO₄: Eu³⁺ thin films [26]. Marisa et al. suggested that the surface energies of the (001) and (112) orientation are lowest in the BaMoO₄ crystal, it indicates that the (004) and (112) texture of the luminescent thin films easier to form [27]. The lower surface energy of (004) will drive the BaMoO₄: Eu³⁺ thin films mounted on (001)-oriented Si substrate with higher orientation.

In order to investigate the effect of texture on luminescence properties, the excitation and emission spectra of nontextured, < 112 >-textured and < 004 >-textured BaMoO₄: Eu³⁺ thin films have been recorded, as illustrated in Fig. 2. It is clearly seen that the excitation spectra of BaMoO₄: Eu³⁺ thin films possess a broad excitation from 280 to 320 nm, which is assigned to the charge transfer of O²⁻ → Mo⁶⁺ in the [MoO₄]²⁻ group and O²⁻ → Eu³⁺ [28]. The excitation peaks at 392, 424, 440 nm and 493 nm corresponding to the transitions of ²F⁰ → ²L₆, ²F⁰ → ²D₅, ²F⁰ → ²D₂, and ²F⁰ → ²D₁, respectively, as shown in Fig. 2a. The emission spectra can be attributed to ⁵D₁ → ⁷F₁, ⁵D₃ → ⁷F₁, ⁵D₅ → ⁷F₂, ⁵D₇ → ⁷F₃, ⁵D₉ → ⁷F₄ transitions, and these spectra peaked at 532, 590, 615, 652, 700 nm, respectively, as shown in Fig. 2b [29]. The narrow peaks at 615 nm have high emission intensity and contribute a lot to the red emission. Compared with nontextured thin films, the < 112 >-oriented and < 004 >-oriented BaMoO₄: Eu³⁺ thin films show higher luminescence intensities. The emission intensity of < 004 >-oriented BaMoO₄: Eu³⁺ thin film is enhanced to 366% compared with the nontextured thin film. This enhanced luminescence intensity of the textured film can be attributed to less lattice mismatch between BaMoO₄: Eu³⁺ thin film and Si substrate.

Fig. 3 shows the SEM images of BaMoO₄: Eu³⁺ thin films, it can be seen the morphology is distinguishing of the < 004 >-textured and < 112 >-textured BaMoO₄: Eu³⁺ thin films. As illustrated in Fig. 3a, b and c, the < 004 >-textured BaMoO₄: Eu³⁺ thin films are composed of smooth spherical particles with uniform size, and the average particle size is 0.53 μm. The BaMoO₄: Eu³⁺ grains are independent and not in contact because the thin film grow perpendicular to the substrate [30,31]. And the smooth surface of the particles also indicates a less lattice mismatch between BaMoO₄: Eu³⁺ thin film and (001)-oriented substrate.

Based on the above comparison analysis, the (001)-oriented Si substrate was exploited as the fixed substrate for mounting a series of BaMoO₄: Eu³⁺ thin films. It is well known that the crystallinity of the thin film is closely associated with the emission intensity, and optimizing the annealing temperature is the most effective way to increase the crystallinity of BaMoO₄: Eu³⁺ thin films. The temperature-dependent emission spectra of BaMoO₄: Eu³⁺ thin films are illustrated in Fig. 4a. The emission intensity reaches its maximum value when the annealing treatment temperature is 700 °C (Fig. 4b), this is consistent with the XRD results. As shown in Fig. 4c, the BaMoO₄: Eu³⁺ thin film annealed at 700 °C shows the best crystallinity and texture quality. In this work, we use a multi-layer film structure to overcome the shortcomings of uncontrollable film thickness and low luminescent efficiency. Fig. 4d and e shows the emission spectra and intensity of BaMoO₄: Eu³⁺ thin films with different layers, the position of the emission peaks is fixed while the intensity is increased gradually. The increased layers are conducive to increasing the emitting volume, resulting in increased emission intensity. As the number of layers increases, the rate of increase in emission intensity gradually slows and reaches saturation. The doping concentration of Eu³⁺ is also strongly related to the luminescence performance of BaMoO₄: Eu³⁺ thin films. As shown in Fig. 4f and g, the emission intensity of BaMoO₄: Eu³⁺ thin films increase first and then decreases, and the optimal doping concentration of Eu³⁺ is 5%. Although the increase in doping concentration will increase in the emission center, a higher doping concentration will result in a closer distance between dopants, which will accelerate the energy transfer between adjacent Eu³⁺. The concentration quenching inevitably occurs when the doping concentration continues to increase.

In order to better understand the excitation and emission process of Eu³⁺ in BaMoO₄, an energy level diagram is illustrated in Fig. 5a. The luminescence decay curves were employed to understand the information of the energy migration among Eu³⁺ ions. The decay curves of BaMoO₄: Eu³⁺ thin films are presented in Fig. 5b. All the samples are well fitted with the biexponential equation below [32,33]:

\[ I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \]

Where \( I(t) \) is the emission intensity corresponding to the time \( t \), \( A_1 \) and \( A_2 \) refer to the constant; \( \tau_1 \) and \( \tau_2 \) are fast and slow fluorescent lifetimes. Further, the average decay time (τ*) can be calculated by the equation as follows:

\[ \tau^* = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2) \]

All the values are summarized in Table 1. The calculated τ* of the
BaMoO₄ thin films with different Eu³⁺ concentration are 663.9, 669.6, 664.9, 656.1, 645.2 μs, respectively. The decay time traces of BaMoO₄: Eu³⁺ thin films are illustrated in Fig. 5c, this reduction in average time (τ*) is the result of the well-known concentration quenching. The distance among Eu³⁺ decreases with increasing doping concentration, resulting in increased nonradiative energy migration.

The Commission Internationale de l’Eclairage (CIE) chromaticity diagram of the optimal BaMoO₄: 0.05Eu³⁺ thin film is displayed in Fig. 6. The color coordinate of this sample is located at (0.6581, 0.3416) and marked as a green star.

The color purity (CP) can be calculated by the following equation [34]:

$$\text{color purity} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\%$$

Where (x, y) presents the coordinate of the sample, (x_i, y_i) stands for the white illumination, (x_d, y_d) corresponds to the dominated wavelength of the sample. The coordinate of the sample is located at the edge of the CIE diagram, indicating that the color purity is close to 100%.

4. Conclusion

In summary, by engineering the grain orientation, we developed a cost-efficiency strategy to fabricate the BaMoO₄: Eu³⁺ thin films on the silicon substrates with controllable surface morphology and highly enhanced luminescence performances, by which the emission intensity of the <004> -textured thin film was enhanced to 366% compared to randomly oriented thin film equivalents. We systematically discussed the influence of the orientation of the substrate, annealing temperatures, layers of thin film, and concentrations of the doping ions on the shape, size, orientation, and photoluminescence performance of the BaMoO₄: Eu³⁺ thin films. With annealing temperature of 700 °C and doping concentration of 5%, the <004> -textured thin film demonstrated red emission at 615 nm with CCT of 2922 °C and ultra-high color purity of nearly 100%. The proposed tactic paves an alternative
Fig. 4. The photoluminescence (PL) spectra and crystal structure of BaMoO$_4$: Eu$^{3+}$ thin films mounted on (001)-oriented Si substrate. (a) The temperature-dependent emission spectra of BaMoO$_4$: Eu$^{3+}$ thin films. (b) The emission intensity of BaMoO$_4$: Eu$^{3+}$ thin films annealed at different temperatures. (c) The XRD pattern of BaMoO$_4$: Eu$^{3+}$ thin films annealed at different temperatures (600, 700, 800 and 900 °C). (d) The layer-dependent emission spectra of BaMoO$_4$: Eu$^{3+}$ thin films. (e) The emission intensity of BaMoO$_4$: Eu$^{3+}$ thin films with various layers. (f) The emission spectra of BaMoO$_4$: Eu$^{3+}$ thin films with various doping concentrations. (g) The emission intensity of BaMoO$_4$: Eu$^{3+}$ thin films with various doping concentrations.

Fig. 5. (a) The diagram of the luminescence mechanism of Eu$^{3+}$ ion-doped BaMoO$_4$ thin films. (b) PL decay curves of BaMoO$_4$: Eu$^{3+}$ thin films with different doping concentration under an excitation wavelength of 300 nm. (c) The decay time traces of BaMoO$_4$: Eu$^{3+}$ thin films.
Table 1
Summary of lifetime fitting parameters of the BaMoO₄: Eu⁺⁺ thin films.

<table>
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<tr>
<th>x</th>
<th>τ₁ (μs)</th>
<th>f₁ (%)</th>
<th>τ₂ (μs)</th>
<th>f₂ (%)</th>
<th>τₑ (μs)</th>
<th>x²</th>
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<td>59.75</td>
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<td>77.88</td>
<td>960.55</td>
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<td>85.59</td>
<td>645.23</td>
<td>2.34</td>
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Fig. 6. CIE chromaticity diagram of Eu⁺⁺ ion-doped BaMoO₄ thin film (annealing temperature = 700 °C, layers = 10, and doping concentration = 0.05).

pathway for preparing high-efficiency luminescent thin films, and shows great potential in endowing luminescent thin film with a wide range of practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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