Applied Surface Science 371 (2016) 391–398

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Upconversion and tribological properties of β-$NaYF_4$:Yb,Er film synthesized on silicon substrate

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A R T I C L E I N F O

Article history:
Received 1 November 2015
Received in revised form
31 December 2015
Accepted 4 March 2016
Available online 7 March 2016

Keywords:
β-$NaYF_4$:Yb,Er upconversion film
Self-assembly
Upconversion luminescence
Tribological property

A B S T R A C T

In this work, β-$NaYF_4$:Yb,Er upconversion (UC) film was successfully prepared on silicon (Si) substrate via self-assemble method for the first time. The chemical composition and surface morphology of the UC film were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), X-ray power diffraction (XRD), and scanning electron microscopy (SEM) measurements. To investigate the effects of KH-560 primer film and chemical reactions on the UC luminescence properties of β-$NaYF_4$:Yb,Er UC film, decay profiles of the 540 nm and 655 nm radiations were measured. Furthermore, tribological test was applied to qualitatively evaluate the adhesion of the UC film. The results indicate that the UC film has been successfully prepared on Si substrate by covalent chemical bonds. This work provides a facile way to synthesize β-$NaYF_4$:Yb,Er UC film with robust adhesion to the substrate, which can be applicable for other UC films.

1. Introduction

Upconversion (UC) material can absorb two or more low energy photons and generate one high energy photon [1,2]. Due to this unique optical property and its potential applications, it has attracted considerable attentions [3,4]. β-$NaYF_4$:Yb,Er UC crystal has been proved as one of the most efficient UC materials to date, many efforts have been done on the synthesis and application of β-$NaYF_4$:Yb,Er crystals [5–7]. However, the applications of bulk crystals are still restricted due to not integrating with UC devices.

Films, which could combine the advantages of bulk materials and the compactness of fibers, have shown potential application prospects in UC devices. Recently, several groups have worked on the fabrication of UC films [8,9]. Moreover, transparent β-$NaYF_4$:Yb,Er UC film has been applied in silicon solar cells to enhance the photovoltaic conversion efficiency [10]. Among the methods used to synthesize UC films, sol–gel method is by far the most commonly reported one [11,12]. However, the sol–gel method requires post-deposition heat treatment to reduce the concentration of quenching –OH oscillators. This may induce the reactions between phosphors and gel, giving rise to unpredictable luminescence properties of the UC film. Furthermore, rational method used to evaluate the performance of UC film is still lacking. So it is of great importance to explore a valid method to prepare β-$NaYF_4$:Yb,Er UC film and a new way to evaluate the film quality.

Self-assembly has always been a facile, simple and convenient technique to chemisorb molecules on substrate surfaces. It has been extensively used to prepare various kinds of films, which exhibit stable chemical and physical properties and strong interfacial binding force with substrates [13–15]. As is known, tribological test is an effective way to investigate the wear resistant property of materials [16,17]. In the service process, failure always happens in films which have weak binding force to substrate and easily fall off from substrate. So when tribological test is applied to films, the tribological results can evaluate the film quality and reflect the interfacial binding force between film and substrate to some extent.

In this work, we aim to provide a facile, simple and convenient way to synthesize β-$NaYF_4$:Yb,Er UC film. The chemical composition of the film and reactions for the related process were investigated in details. UC luminescence properties of the as-prepared UC film were also studied. Tribological test was used to evaluate the quality of UC film and detect the interfacial binding force between film and Si substrate. The results demonstrate that the β-$NaYF_4$:Yb,Er UC film has been successfully synthesized and exhibits strong UC luminescence and robust adhesion to the substrate.

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http://dx.doi.org/10.1016/j.apsusc.2016.03.035
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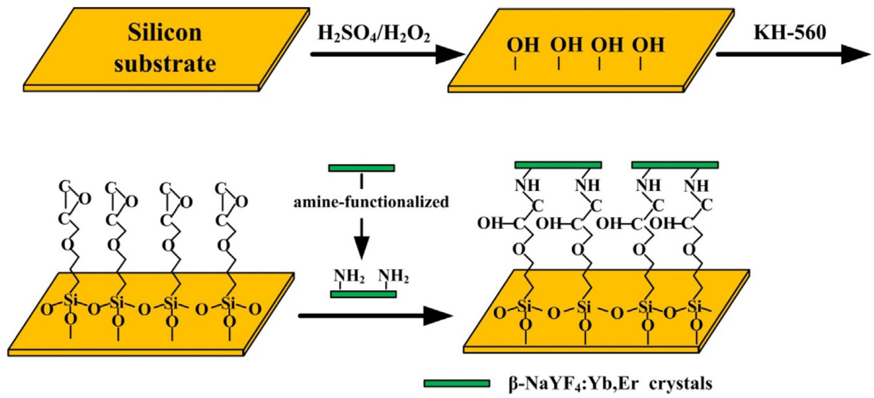

Fig. 1. Proposed schematic view for the assembly of β-$NaYF_4$:Yb,Er UC film on Si substrate.

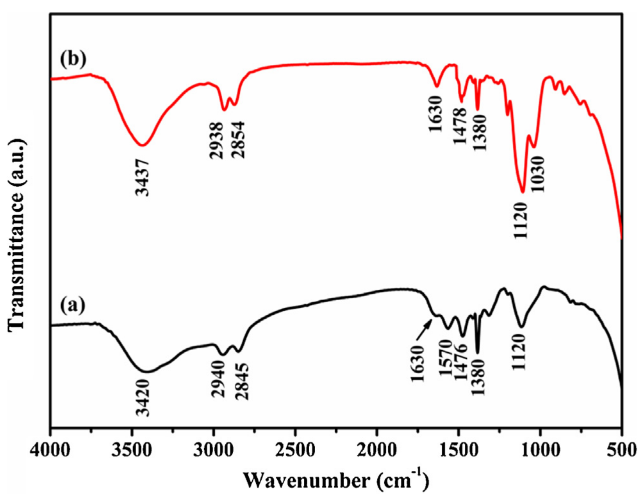

Fig. 2. FTIR spectra of the amine-functionalized β-$NaYF_4$:Yb,Er crystals (a) and β-$NaYF_4$:Yb,Er crystals after reacting with KH-560 (b).

2. Experimental

2.1. Materials

All utilized chemicals including Polyethylenimine (PEI, 70000, 50 wt%), γ-(2,3-epoxypropoxy) propyltrimethoxysilane (KH-560), and Rare-earth nitrates ($Y(NO_3)_3{\cdot}6H_2O$, $Yb(NO_3)_3{\cdot}5H_2O$, $Er(NO_3)_3{\cdot}5H_2O$) of 99.99% purity were purchased from Aladdin Industrial Corporation (Shanghai). Other reagents of analytical grade were used directly without further purification. Deionized water (>18.2 MΩ) was used throughout the experiment. PEI stock solution (5 wt%) was obtained by dissolving PEI in deionized water.

2.2. Synthesis of amine-functionalized β-$NaYF_4$:Yb,Er crystals

In a typical procedure for preparation of β-$NaYF_4$:Yb,Er crystals, 7.8 ml $Y(NO_3)_3$ (0.1 M), 2 ml $Yb(NO_3)_3$ (0.1 M), 2 ml $Er(NO_3)_3$ (0.01 M), 1 mmol NaCl and 10 ml PEI solution (5 wt%) were firstly mixed together with magnetic stirring for 30 min to form a homogeneous solution. Then 12 ml NH_4F solution (1 M) was added to the mixture. Finally, the mixture was stirred for another 30 min and transferred to a 50 ml autoclave, sealed, and maintained at 180 °C for 24 h. After the autoclave was cooled down naturally to room temperature, the crystals were deposited at the bottom of the vessel. The crystals were purified by centrifugation and washed with ethanol for several times, dried at 60 °C for 12 h.

Table 1
WCAs of different samples.

Samples	Si/SiO_2	KH-560 film	β-$NaYF_4$:Yb,Er crystals	β-$NaYF_4$:Yb,Er UC film
WCA/deg	~0	55.1 ± 2.2	74.5 ± 3.1	83.2 ± 2.1

2.3. Pretreatment of Si substrate wafers

Si wafers (cut in size of 10 mm × 10 mm) were ultrasonic cleaned by acetone, ethanol and water in sequence for 10 min. Then those wafers were immersed into piranha solution (a mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) for surface hydroxylation at 90 °C for 1.5 h. Then the wafers were rinsed with deionized water and dried under nitrogen flow.

2.4. Synthesis of self-assembled KH-560 film on Si substrate

5% (vol/vol) KH-560 solution was prepared by adding KH-560 into the mixture of methanol and water (volume ratio of 5:1) and stirring for 5 min. The KH-560 was considered to dissolve and hydrolyzed in this procedure. The hydroxylated Si wafers were immersed into the above solution for 30 min. Then the wafers were taken out and cleaned by methanol for 3 times, dried by nitrogen flow.

2.5. Self-assembly of β-$NaYF_4$:Yb,Er UC film

Si substrate wafers from the last step were immersed in a solution of β-$NaYF_4$:Yb,Er crystals (0.05 wt%) for 20 h at 60 °C. Then the wafers were cleaned by deionized water for several times and dried at 80 °C for 2 h. For comparison, the hydroxylated Si substrate wafers from Section 2.3 without KH-560 primer film were assembled with β-$NaYF_4$:Yb,Er crystals by the same method.

2.6. Characterization

Water contact angle (WCA) of the coated surface was measured by a DSA 100 contact angle meter (Kruss, Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-6700 spectrometer from Thermo Fisher. The binding energy state and element composition of films were detected by X-ray photoelectron spectroscopy (XPS, Kratos, AXIS ULTRA DLD). X-ray power diffraction (XRD) measurement was performed on a Bruker D8-Advance diffractometer with Cu Kα radiation (λ = 0.154 nm). The 2θ angle ranges from 10° to 70° at a scanning rate of 4°/min. The size and morphology of as-prepared β-$NaYF_4$:Yb,Er crystals were observed by a 120 KV biological transmission electron microscope (B-TEM; FEI, Tecnai G2 Spirit Biotwin). Morphology observation of KH-560 film was conducted by atomic force