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Microstructure and multiphoton luminescence of Au nanocrystals prepared by using glancing deposition method

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Abstract

Au crystal columns embedded in SiO_2 with an average length of 480 nm and diameter of 30 nm were prepared by radio frequency co-sputtering technique with glancing angle. The photoluminescence (PL) of the Au–SiO_2 crystal column film exhibited polarization characteristic. With an increase of the laser power, the slope $\partial \log(\text{PL intensity})/\partial \log(\text{laser power})$ changed from 2 to 3, which indicated that the PL of Au–SiO_2 crystal columns were induced by two- and three-photon absorption, respectively.

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Keywords: Photoluminescence; Multiphoton luminescence; Au–SiO_2 crystal columns

1. Introduction

The noble metal columnar thin film, prepared by oblique deposition, was first reported in 1989 [1] and similar results with a glancing angle deposition were obtained by Robbie and co-workers [2,3]. Films with large third-order optical nonlinearity and other optical properties have attracted much attention [4–6] owing to their applications in numerous aspects of physics and biology [7], such as optical polarizers [8], high birefringence biaxial films [2], thin-film wave plates [9], magnetic storage media [10,11], nanoemitters [12], and actuators [13]. The photoluminescence (PL) from the films can be adjusted by controlling their microstructures, which includes rods [3], spheres [14,15], plates [16], zigzags [3,17], pillars [18], chevrons [11,19], spirals [20], and Y shapes [21].

Visible PL from noble metal films was first reported in 1969 [22], and two-photon-induced PL (2PI-PL) from noble metal particles was first obtained in silver [23]. Boyd et al. [24] reported 2PI-PL from gold nanoparticles for the first time. 2PI-PL and three-photon-induced PL (3PI-PL) from silver and gold nanoparticles were investigated by Fourkas and co-workers [25,26]. The PL of resonant optical antennas, consisting of gold nanorods, involving a four-photon interaction was reported in 2005 [27]. Both the density of states and the field enhancement effects played important roles in the process of multiphoton-induced PL [26,28,29]. Recently, Wang et al. [30] reported highly efficient avalanche multiphoton luminescence (MPL) from ordered-arrayed gold nanowires. However, MPL from Au:oxide composite films prepared by radio frequency (r.f.) sputtering technique with glancing angle was seldom reported.

In this letter, we prepare columnar thin films by r.f. sputtering technique with glancing angle and composite target. The films are composed of crystal columns. The PL emission of the Au–SiO_2 crystal columns films shows polarization characteristic. Furthermore, as the laser power

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increases, the Au–SiO_2 crystal column film luminescence can be excited by the absorption of 2–3 photons. Based on these new characters, it can possibly be used in optical, chemical, and biological devices.

2. Experimental procedures

The Au–SiO_2 crystal column films were deposited at room temperature by using r.f. co-sputtering technique with Au and silicon dioxide compound target, the target–substrate distance was about 27 mm, the sputtering gas was Ar with a purity of 99.99%, and the sputtering pressure was about 7.5 Pa. The sputtering power was 165 W. The Au atom concentration of samples was 74% and the sputtering oblique angles θ were 0° and 80°, respectively, as shown in Fig. 1. The structure of the films was investigated by a scanning electron microscope (SEM, SIRION-FEG). As shown in Fig. 2(b), we could find that the films were rimous and composed of columns, which were due to atomic shadowing effects [31]. When the incident sputtering angle θ increased from 0° to 80°, the columns inclined toward the target (shown in Figs. 2(a) and (c)). The microstructure and diffraction ring of a single Au–SiO_2 crystal column was investigated by transmission electron microscope (TEM, JEOL-2010HT, as shown in Fig. 3(a)) and X-ray diffraction (XRD); the average column length was 480 ± 20 nm, and the diameter was about 30 nm. The transmittance spectra measurements were carried out using a UV–vis–NIR spectrophotometer (Varian, Cary 5000); the PL spectra were investigated by monochromator (Spectrapro 2500i, Acton) with a liquid nitrogen cooled CCD detector (SPEC-10, Princeton), and the excitation source for PL was a picosecond (ps) Ti:sapphire laser (Mira 900, Coherent) with a pulse duration of 3 ps and repetition rate of 76 MHz. The PL of samples was obtained by reflection measurement, the laser beam was filtered by long wave pass filter (LWPF), and passed through the neutral density filter (NDF), half-wave plate (HWP), and lens (the focal length of lens was 70 mm), and excited on the sample at an incident angle of 67°. The luminescence from the sample was collected by the

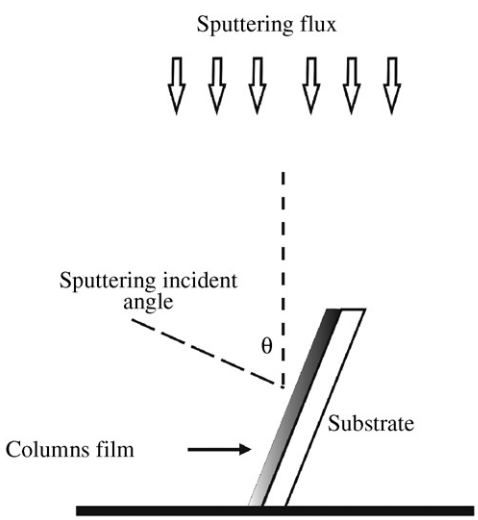

Fig. 1. Radio frequency (r.f.) sputtering technique with glancing angle.

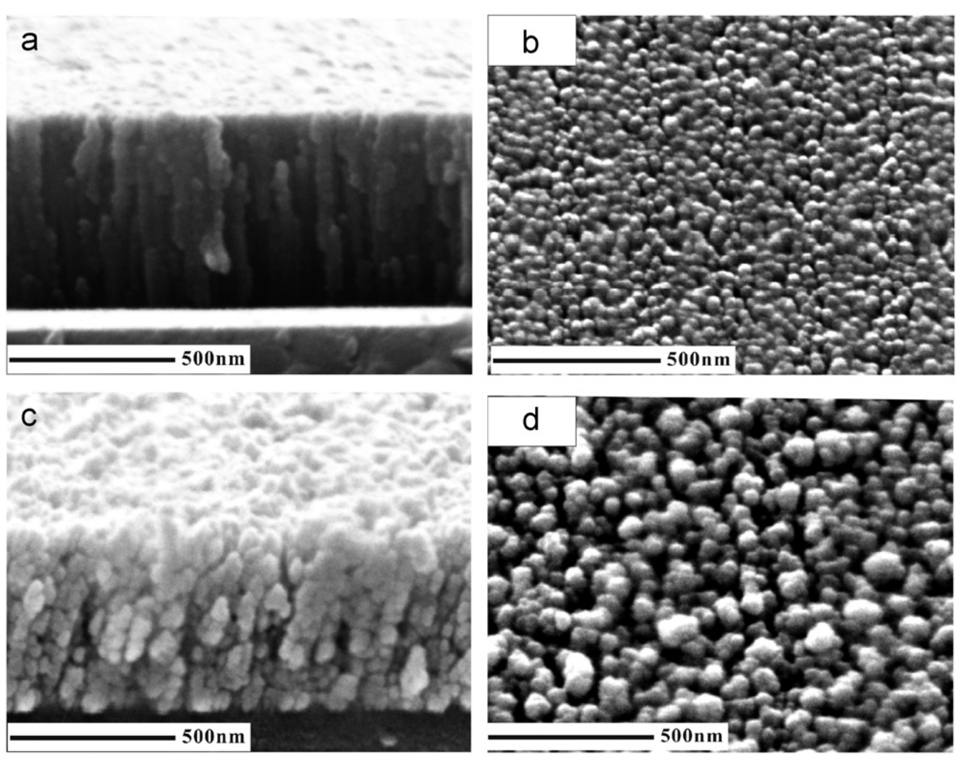

Fig. 2. SEM images of the Au–SiO_2 film with $\theta = 0°/80°$ deposited at the sputtering pressure 7.5 Pa; (a) and (c) are cross-section images; (b) and (d) are surface images.