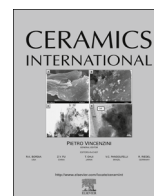




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# Photoactivity enhancement of zinc sulfide ceramics thin films through ultrathin buffering engineering



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## ABSTRACT

Zinc-sulfide (ZnS) thin films 200 nm-thick with various crystal features were fabricated using RF sputtering onto patterned sapphire substrates with and without ultrathin homo-ZnS and hetero-zinc oxide (ZnO) ultrathin buffer layers (approximately 45 nm in thickness). Microstructural analyses revealed that the crystalline ZnS thin films with a columnar grain feature were deposited on the various ultrathin buffer layers-coated substrates through RF sputtering. The surface morphology of the ZnS thin films became rough and the crystal defect density of the ZnS thin films increased when the ZnS thin films were grown on the buffer layers. Comparatively, the rugged and island-like ZnO buffer layer engendered the crystal growth of the ZnS thin film with a higher degree of structural disorder than that of the crystal growth on the ZnS buffer layer. An increased crystal defect number together with the highly rugged film surface of the ZnS thin film buffered with ultrathin ZnO layers efficiently enhanced the photoactivity of the 200 nm-thick ZnS thin film in this study.

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## 1. Introduction

Zinc sulfide (ZnS) is a semiconductor with a wide direct bandgap value in the UV light region [1–4]. It possesses two stable cubic and hexagonal crystal structures, with bandgap values of approximately 3.54 eV and 3.80 eV, respectively [5,6]. ZnS has a variety of scientific applications such as photocatalysts, phosphors, and gas and humidity sensors because of its variety of physical properties [1,3,7,8]. Among its various material dimensions, ZnS in the form of two-dimensional thin film is highly desired for application in scientific devices. Various chemical and physical methods have been developed for the preparation of ZnS thin films, such as chemical vapor deposition [6], chemical bath deposition [9], thermal evaporation [10], sputtering [11], and electrodeposition [12]. However, most chemical synthesis methods for preparing ZnS thin films are difficult for controlling the thickness of film with high homogeneity, maintaining low morphology deviation over the film surface, and maintaining a high degree of thin-film step coverage. By contrast, sputtering techniques have several advantages. For example, such techniques are feasible for large-area thin-film coating and feature easy thin-film microstructure control, high film-thickness homogeneity, high repeatability, and easy control of thin-film compositions, and can be integrated into industrial semiconductor processes [13–15].

Therefore, preparation of ZnS thin films through sputtering that yields satisfactory properties is highly desired for device applications.

Improvement of the photoactivity of wide bandgap semiconductors is becoming crucial for developing them for various photoactivated device applications. The control of material microstructures is particularly critical for designing thin-film semiconductors with satisfactory light harvesting efficiency. The crystallinity, surface area, and defect density are believed to affect the photoactivity of ZnS [16]. Several studies have focused on the photoactivity of ZnS in forms of nanostructures or particles with various sizes and shapes [8,17,18]. Although these studies have shown that ZnS nanostructures can display satisfactory photoactivities with microstructural modifications, their complex synthesis and incompatibility with industrial semiconductor processes for synthesizing nanostructured ZnS still hinder the applications of nanostructured ZnS in actual photoactivated devices. By contrast, studies on improving the photoactivity of ZnS thin films are crucial for realizing such thin film material in various photoactivated device applications. However, related research on enhancing the photoactivity of various ZnS thin films is still limited. In this study, ZnS thin films were prepared through RF sputtering on patterned sapphire substrates with and without various ultrathin buffer layers. A concept for designing ZnS thin films that improves photoactivity through proper ultrathin layer buffering is described herein. Structural modifications of ZnS thin films through ultrathin buffering engineering are proposed. The correlation between the microstructures and photoactivity of the ZnS

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thin films with and without various ultrathin buffer layers was systemically investigated in this study.

## 2. Experimental

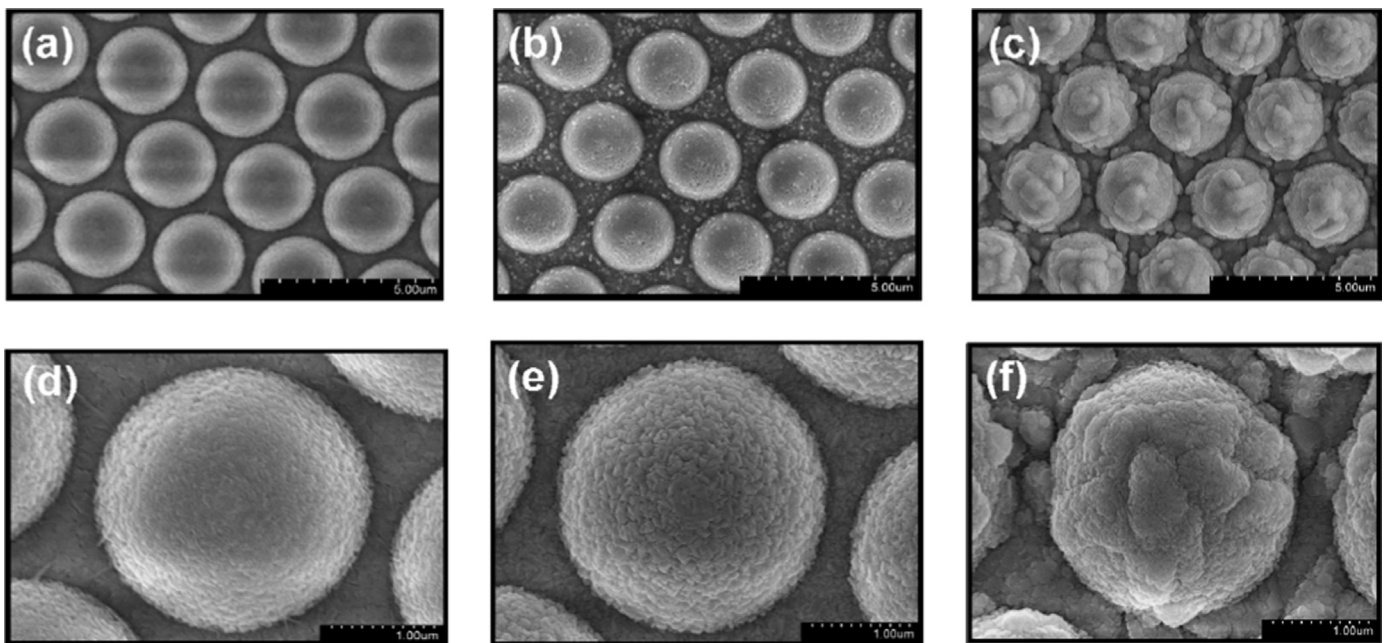
ZnS thin films were grown on patterned c-axis-oriented sapphire substrates with and without ultrathin buffer layers, using RF magnetron sputtering. The thickness of the ZnS thin films were fixed at approximately 200 nm and the growth temperature was maintained at 460 °C. The working pressure of deposition was fixed at 2.67 Pa, using pure argon gas for the films. Moreover, the thin film growth conditions for the ultrathin ZnS buffer layer are the same as those of the 200 nm-thick ZnS thin films. The ultrathin ZnO buffer layer was prepared at 375 °C with the working pressure of 2.67 Pa, using an Ar/O<sub>2</sub> ratio of 4:1 for the ZnO buffer layer. The ultrathin ZnO and ZnS thin films used as buffer layers have a film thickness of approximately 45 nm. Before the 200 nm-thick ZnS films were grown on the ZnS and ZnO buffer layers-coated substrates, the ZnO and ZnS buffer layers were preannealed at 600 °C for 30 min in air and vacuum ( $6.67 \times 10^{-4}$  Pa) atmospheres, respectively.

The crystal structures of the samples were investigated using X-ray diffraction (XRD; Bruker D2 PHASER), applying Cu K $\alpha$  radiation. The surface morphology of the ZnS films was determined using scanning electron microscopy (SEM; Hitachi S-4800). The detailed microstructures of the as-synthesized samples were characterized using high-resolution transmission electron microscopy (HRTEM; Philips Tecnai F20 G2). Thin slices of the ZnS thin film samples for cross-sectional TEM analysis were prepared using a dual-beam focused-ion-beam instrument (FIB; FEI Nova 200). The room temperature-dependent photoluminescence spectra were captured using the 325 nm line of a He–Cd laser (PL; HORIBA HR800). The optical absorbance spectra of the samples were recorded by using UV-Vis spectrophotometer (Jasco V750). Photocatalytic activity of ZnS thin films were performed by comparing the degradation efficiency of aqueous solution of methylene blue (MB;  $10^{-6}$  M) with various CdS thin-film samples as catalysts

under solar light irradiation at various durations. The thin-film sample size for the tests of photodegradation of MB solution is fixed at 1.5 cm  $\times$  1.5 cm in this work.

## 3. Results and discussion

Fig. 1(a)–(c) display the SEM images of the ZnS thin films grown on the patterned sapphire substrates with and without ultrathin buffer layers. The ZnS thin films formed separated and ordered bump-like crystals arranged over the substrates. The surface morphologies of the ZnS thin films differed according to the buffer layer on which they were grown. The surface of the ZnS thin films grown on the substrate without buffer layers was dense and comprised tiny grains (Fig. 1(d)). Comparatively, the surface morphology of the ZnS thin films became visibly and irregularly granular with a larger surface crystallite size when the film was grown on the ultrathin ZnS buffer layer. The surface of the ZnS thin film consisted of numerous tiny grooves and most of the surface grains were approximately 100–140 nm in size (Fig. 1(e)). Furthermore, a considerable increase in surface roughness was observed in the ZnS thin film grown on the ultrathin ZnO buffer layer (Fig. 1(f)). Clear three-dimensional bump-like grains covered the surface of the ZnS thin film grown on the ZnO-buffered substrate. The surface of these grains was uneven and comprised tiny crystallites. These surface bump-like grains were approximately 600–800 nm in size. Fig. 2(a)–(c) display the XRD patterns of the ZnS thin films grown on the substrates with and without ultrathin buffer layers. Fig. 2(a) shows a sharp Bragg reflection originating from the cubic ZnS (111) and a weak Bragg reflection from the hexagonal ZnS (100) (according to JCPDS No. 005-0566 and No. 005-0492, respectively), confirming that the ZnS thin film grown without any buffer layers was polycrystalline with mixed crystallographic structures; moreover, the ZnS thin film exhibited a highly crystalline quality. Similar mixed phases of the zinc blend cubic and wurtzite hexagonal structures for the ZnS in forms of thin films and nanostructures have been prepared through vacuum processes with a growth temperature lower than 750 °C



**Fig. 1.** SEM micrographs of the ZnS thin films with and without ultrathin buffer layers: (a) ZnS film grown without buffer layer. (b) ZnS thin film grown with the ultrathin ZnS buffer layer. (c) ZnS thin film grown with the ultrathin ZnO buffer layer. (d) The corresponding high-magnification image of figure (a). (e) The corresponding high-magnification image of figure (b). (f) The corresponding high-magnification image of figure (c).

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