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Novel Crystal Phase of Tin Nitride Synthesized by Reactive Sputtering

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Abstract

Artificially synthesized tin nitride (SnN) has been reported to have a spinel Sn_3N_4 crystal structure. In this study, SnN thin films with a novel crystal phase were synthesized at a substrate temperature of 723 K via a reactive sputtering process. Quantification analyses using X-ray photoelectron spectroscopy revealed that the N/Sn ratio of the SnN film surface was 0.92. The peaks observed in the X-ray diffraction (XRD) profile did not match patterns of any tin-related materials. Based on the XRD fitting simulation, we determined that the SnN films have a zincblende-type crystal structure, making it the first experimental report on the binary systems of nitrogen and group 14 elements. The fundamental electrical, optical, and mechanical properties of the SnN films were characterized, and potential applications of the novel SnN phase were discussed.

Keywords: Tin nitride, magnetron sputtering, crystal structure, X-ray photoelectron spectroscopy, X-ray diffraction,

1. Introduction

Tin belongs to group 14 elements and has been utilized by human beings for a long period for various applications. However, compared with alloys and oxides of tin, the physical and chemical properties of tin nitride (SnN) compounds have rarely been investigated. A crystalline SnN material was initially reported by Lima et al. as magnetron-sputtered SnN films [1], followed by studies that examined the properties of films synthesized by the same process [2–7]. The chemical vapor deposition process has also succeeded in the preparation of polycrystalline SnN films [8–11]. Concerning the application of SnN thin films, studies have investigated their electrochromic behavior [12], including the feasibility for optical recording media [4, 13], protein-binding properties for biochips [14–15], electrode characteristics in thin-film batteries [16], and a candidate for green photovoltaic materials [17].

In 1999, Scotti et al. reported the crystal structure of a SnN compound obtained by the reaction of SnI_4 with KNH_2 in liquid ammonia [18]. Using neutron and X-ray diffraction (XRD), they determined that the crystal structure of the polycrystalline SnN was cubic spinel Sn_3N_4 (space group (SG) #216, $Fd\bar{3}m$), which had been previously described as a hexagonal system [1–11, 13]. They also investigated the Sn–N bonding structures via transmission-mode X-ray absorption fine structure experiments [19]. After the crystal structure was determined, a rapid synthesis of spinel Sn_3N_4 by solid-state metathesis reactions was recently reported [20]. Shemkunas et al. measured the mechanical properties of spinel Sn_3N_4 using a nanoindentation technique [21]. Additionally, theoretical calculations on the structure and properties of spinel Sn_3N_4 have been carried out [22]. Huang and Feng examined polymorphs of spinel Sn_3N_4 and determined that $CaFe_2O_4$- and $CaTi_2O_4$-type crystal structures can be expected to be high-pressure phases [23]. To the best of our knowledge, there are no reports in the literature on the successful synthesis of any polymorphs of the spinel Sn_3N_4 phase.

In this paper, we report the synthesis of a novel crystal phase of SnN films synthesized by reactive radio frequency (RF) magnetron sputtering at a substrate temperature of 723 K. We refer to this crystal phase as the high-temperature phase of SnN

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