Thin Solid Films 571 (2014) 84–89

Contents lists available at ScienceDirect

Thin Solid Films

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

# Tin nitride thin films fabricated by reactive radio frequency magnetron sputtering at various nitrogen gas ratios

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ARTICLE INFO

*Article history:*
Received 12 December 2013
Received in revised form 2 October 2014
Accepted 6 October 2014
Available online 15 October 2014

*Keywords:*
Tin nitride
X-ray photoelectron spectroscopy
Contact angle
Surface free energy
Sputtering
X-ray diffraction

ABSTRACT

Sn nitride thin films are remarkable materials that can be implemented in applications such as microelectronic devices and recording media. This paper presents the analysis of the various Sn nitride thin films' structural, electrical, and chemical properties using a surface profiler, X-ray diffraction, a 4-point probe, X-ray photoelectron spectroscopy (XPS), and distilled water and ethylene glycol contact angle measurements. The Sn nitride thin films were prepared via radio frequency magnetron sputtering. The thickness of Sn nitride thin films decreased in the regions where $N_2$ gas ratios ranged from 20% to 100%. The surface resistance decreased from $6.34 \times 10^4$ to 56.2 Ω/sq with gradual increasing of $N_2$ gas ratios from 20% to 100%. Change in crystallinity of the films was observed as $N_2$ gas was progressively introduced, from metallic Sn to the amorphous Sn nitride phase. The high resolution XPS spectra indicates that the intensity of $Sn^{2+}$ increased, while those of $Sn^{4+}$ and $Sn^0$ decreased with increasing $N_2$ gas ratios, confirming the bond formation of Sn and N. The total surface free energy (SFE) varied by changing the $N_2$ gas ratio. When the $N_2$ gas ratio in the sputter gas was low (less than 20%), the dominant contributing factor to the total SFE switched from polar to dispersive SFE. In samples where the $N_2$ gas ratio was over 20%, the major contribution to the total SFE was dispersive SFE.



## 1. Introduction

Metal nitride thin films are materials that have been attracting immense attention in the scientific community because of their interesting electrical and optical characteristics. The chemical bond strength of the metal-nitrogen leads to their stability to be used in extreme environments [1]. Metal nitride thin films, which have a wide range of band gap variability, have been utilized in many applications such as laser and blue and ultraviolet light emitting diodes [2,3]. Among the metals forming nitride thin films, group IV metals have been earning the most attention in technological applications. Silicon nitride and germanium nitride have been used in microelectronic devices and insulators [4]. Although Sn nitride has electrochromic and semiconducting properties, Sn nitride has not been extensively investigated and there are few literature published on the regarding material [5]. Due to the characteristics of Sn nitride, it could be used in a variety of applications, such as microelectronic devices and recording media [1,4,6]. Scotti et al. obtained $Sn_3N_4$ (spinel structure) from $SnI_4$ and $KNH_2$ after annealing for 2–5 days at 573 K and confirmed tin nitride with X-ray powder diffraction [7]. Lützenkirchen-Hecht et al. synthesized $Sn_3N_4$ with $SnBr_2$ and $KNH_2$ with mole ratio of 1:2. They verified that the oxidation state of Sn in tin nitride with extended X-ray absorption fine structure study was 4 [8]. Numerous methods to synthesize metal thin films are known such as atmospheric pressure chemical vapor deposition (CVD) [1,2,6,9], plasma-enhanced CVD [10], magnetron sputtering [11,12], reactive sputtering [13,14], and reactive radio frequency (RF) sputtering [3,5,15,16]. Among them, reactive RF magnetron sputtering is commonly used to obtain uniform thin films. The chemical and physical properties of the thin films are affected by various deposition conditions: the working pressure, the kinds of sputtering gas, the RF power, and the temperature of the substrate. In order to obtain metal nitride thin films, the parameters must be controlled. In this research, we fabricated Sn nitride thin films by reactive RF magnetron sputtering with different $N_2$ gas ratios and investigated their structural, electrical, chemical properties, and surface free energy by means of surface profiler, X-ray diffraction (XRD), 4-point probe, X-ray photoelectron spectroscopy (XPS), and distilled water and ethylene glycol contact angle measurements.

## 2. Experimental details

Sn nitride thin films were deposited on silicon (100) substrate by reactive RF magnetron sputtering using a metallic Sn target (Tasco, Korea, 99.99%) in a mixture of high purity Ar and $N_2$ gases. Ar gas was used as the sputter gas and $N_2$ gas was used as the reactive gas. The Si substrate was cleaned with acetone and diluted HF before placing it in the sputtering chamber. The base pressure of the sputtering chamber was maintained below $4.8 \times 10^{-4}$ Pa and the working pressure was kept

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http://dx.doi.org/10.1016/j.tsf.2014.10.035
0040-6090/

at $1.5 \times 10^{-1}$ Pa by a turbo molecular pump (TMP) and a roughing pump (RP). The total gas flow rate of Ar and $N_2$ gas was fixed at 30 sccm and the fraction of $N_2$ gas in the total gas range was varied from 0 to 100%, which was manipulated by a separated mass flow controller. Sn nitride film obtained at X% of $N_2$ in the sputter gas will be addressed as SnN-X here on after. The applied RF power on the Sn target was maintained at 200 W during the deposition process. Pre-sputtering was performed for 1 min prior to each of the deposition process and the deposition time was kept for 10 min. The chemical environment of the obtained films was investigated with X-ray photoelectron spectroscopy (XPS, ESCALab MKII, VG, UK) with an Al Kα X-ray source (1486.6 eV). The base pressure of the XPS analysis chamber was low: in the $1.3 \times 10^{-8}$ Pa range, which was achieved by a TMP, a RP, two ion pumps, and a Ti-sublimation pump. The Sn nitride thin films were cleaned with Ar-ion sputtering process prior to taking XPS spectra. Ar-ion sputtering was performed at $4.0 \times 10^{-5}$ Pa of Ar for 3 min, beam energy of 5 keV and the target current was 1.6 μA. The high resolution XPS spectra were taken with a concentric hemispherical analyzer in constant analyzer energy mode. XPS spectra were obtained from the Sn nitride films with $9 \times 9$ mm$^2$ of size and the take off angle of the photoelectron was set to normal with respect to the electron energy analyzer. High resolution XPS spectra were obtained after nine scans to increase signal to noise ratio. The obtained spectra were deconvoluted with XPSPEAK software (ver 4.1) in the 30% of Gaussian/Lorentz ratio to verify the chemical environment of Sn and N and FWHM was 2.0 eV for Sn and 2.1 eV for O 1s. The crystallinity of the films was evaluated with X-ray diffraction (XRD, X-pert pro, Netherlands) which was operated with 0.1 eV of energy step, 40 kV of acceleration voltage, and 30 mA of filament current using a Cu Kα (0.15 nm) source. More than 10 trials of measurements were made for the thickness of Sn nitride thin films measured through a surface profiler (Alpha-Step 500, Tencor, USA). In order to measure the film thickness, the edge of the Si substrate was covered with Kapton tape before sputtering. The surface resistance and other electrical properties were measured by means of the 4-point probe method (MCP-T6000, Loresta, Netherlands). Contact angles of the thin films were measured with distilled water (DW) and ethylene glycol (EG) to estimate the surface energy and hydrophilicity by using a home-made contact angle measurement system.

## 3. Results and discussion

The thickness of Sn nitride thin films was measured by a surface profiler as shown in Fig. 1. The thickness of the films increased from 0 to 20% of $N_2$ gas ratio in the sputter gas (region 1) and then decreased until 100% of $N_2$ gas ratio (region 2). From the thickness and deposition time, the deposition rate of Sn nitride thin films was obtained. The largest and the smallest values of deposition rate were 12.92 and 3.30 nm/min for SnN-20 and SnN-100, respectively. The sample notation shown in the figures, such as SnN-10 means Sn nitride thin films obtained with 10% of $N_2$ gas ratio. In region 1, the thickness of the films was increased. This result was the opposite of what we expected because the sputter gas ratio decreased in this range. The increase of thickness could be caused from the dominant structure of the thin films. The dominant phase in region 1 was metallic Sn and the amorphous Sn nitride started to grow from 10% of $N_2$ gas ratio. The $N_2$ gas in region 1 was not enough to fully grow Sn nitride films without the formation of metallic Sn phase. Therefore, the film was heterogeneously packed with metallic Sn and amorphous Sn nitride phases. This phenomenon was confirmed by XRD; metallic Sn phases remained until 20% of $N_2$ gas ratio shown in Fig. 2(a). Thus, the film growth of SnN-10 and SnN-20 can be considered as a loosely packed structure compared to SnN-0 because of the coexistence of metallic Sn and Sn nitride phases in SnN-10 and Sn-N-20 shown in Fig. 2(b) [17,18]. More than 30% of $N_2$ gas ratio, the decrease of thickness can be well explained by the ratio of sputter gases employed during the deposition. As the $N_2$ gas ratio increased, the sputter yield of Sn decreased [19]. There was no phase mixing like SnN-10 and SnN-20 in region 2. Therefore, the thickness of thin films gradually decreased with increasing $N_2$ gas ratio.

The XRD diffractograms of Sn nitride thin films with respect to $N_2$ gas ratio and representative deconvoluted XRD diffractograms are shown in Fig. 2(a) and (b), respectively. The peaks at the diffraction angles of 30.8°, 32.1°, 43.8°, and 44.9° were assigned to (200), (101), (220), and (211) of metallic Sn with tetragonal phases, which were observed in region 1. A broad peak centered at about 30° of diffraction angle started to evolve from SnN-10 shown in Fig. 2(b). With increasing $N_2$ gas ratio to 20%, the peak intensities of (101) and (211) decreased and those of (200) and (220) increased. This implies that the dominant phase of metallic Sn could be controlled by $N_2$ gas ratio. The crystal sizes of metallic Sn were deduced from the Sn(101), (200), (220) and (211) peaks using the Debye–Scherrer's equation [20] and are listed in Table 1. Based on these determined values, the crystal size decreased with increasing $N_2$ gas ratio. From SnN-30, no distinct metallic Sn phases were observed and only one broad peak at about 30° was detected. This broad peak is caused from the amorphous phase of Sn nitride [21]. The phase transformation from metallic Sn to Sn nitride was controlled by changing the $N_2$

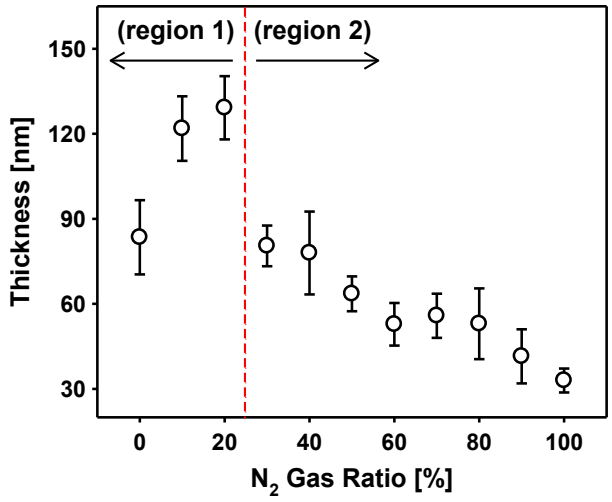


**Fig. 1.** Thickness of Sn nitride thin films deposited from 0 to 100% of $N_2$ gas ratios.

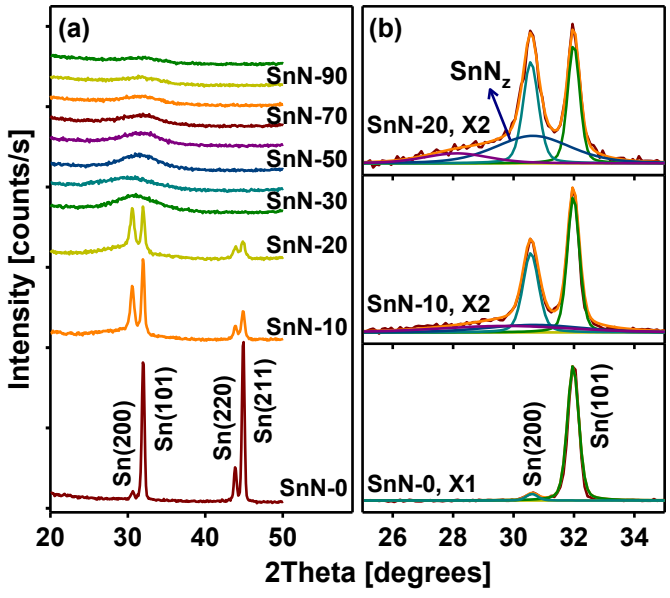


**Fig. 2.** (a) X-ray diffraction patterns of Sn nitride thin films with respect to $N_2$ gas ratios. (b) Deconvoluted diffractograms of Sn(101) and (200) phases from 0 to 20% of $N_2$ gas ratios.