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# Ferromagnetic ordering and metallic-like conductivity in sputtered $SnN_x$ films

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ABSTRACT

Polycrystalline $SnN_x$ films were fabricated by reactive sputtering with various substrate temperatures. The film has a hexagonal tin-rich structure and decomposition temperature is above 500 °C. The band-gap enlarged to 3.10 eV due to the complex defects and the conductivity of the films shows metallic-like behavior, which has the opposite variation trend with ferromagnetism as the substrate temperature changes. The origin of ferromagnetism may be from the intrinsic point defects, which result in a net moment by unpaired spin electrons. The feeble coercivity with no obvious magnetocrystalline anisotropy suggests that the magnetism in our samples is not a bulk effect, and it distributes unevenly in the grain boundaries or interfaces. Furthermore, thermal decomposition also has significant influence on the magnetic and transport properties.



## 1. Introduction

Tin nitride ($SnN_x$) is one of the group IV nitrides with special interest for applications in microelectronic devices, and it has been proposed as material for optical switching devices and optical recording media due to the promising semiconducting and electrochromic properties [1–3]. The thermal instability suggests the possible use of $SnN_x$ in metallization reactions that could be of importance for the electronic industry. Fisher and Iliovichi gave the first indication of a compound $Sn_3N_4$, which would decompose at 360 °C [4]. Since then, a number of experimental studies have been carried out to understand the properties of this compound. So far, tin nitride in powder, thin film and nanostructure forms have been prepared by various methods [5–9]. Depending on the details of the preparation procedures, amorphous as well as crystalline structures with varying atomic concentrations of Sn and N have been reported. Moreover, the band-gap of the tin nitride films changes from 1.5 to 4.9 eV depending on the growth method and condition [8,10]. Maruyama and Morishita studied the dependence of various physical properties of polycrystalline tin-nitride films, demonstrating that the films decomposed into the elements at 550 °C and reached the maximum decomposition rate at 615 °C [3]. Lima et al. investigated the crystal structure and chemical composition of polycrystalline tin-nitride films prepared by reactive magnetron sputtering and found the films had a C6 hexagonal structure isomorphous to $Ca(OH)_2$ with a tin-rich composition [7], due to the difficulty of preparing order sample with stoichiometric Sn:N ratios.

In addition, for the aim of combined nonvolatile magnetic storage and conventional semiconductor electronics, previous studies have been focused on dilute magnetic semiconductors (DMS), in which the magnetic moments are induced by doping magnetic transition-metal (TM) ions [11,12]. More recently, theoretical calculations demonstrated that long-range ferromagnetism (FM) order could exist in some undoped semiconductors [13,14]. Besides, magnetic ordering in nitride semiconductors, such as InN, AlN and BN, has been also reported and intrinsic point defects may be the origin of the FM [15–17]. Generally, the semiconductors with anionic defects are promising candidates and more facile to achieve because the induced localized magnetic moments by cation vacancies are limited by the high formation energy [18]. In contrast to group III-N compound semiconductors there are few investigations on the spin polarization charge of group IV-N compound semiconductors. Since the low formation energy of nitrogen vacancy ($V_N$) in $SnN_x$ which favors a tin-rich composition [7], it is outstanding in the aspect of electrical conductivity and interesting to test the possibility of using defects as native "dopants" than TM dopants to induce FM order in $SnN_x$ materials for the applications in spintronics devices. In this paper, we investigated the structure, optical, magnetic and transport properties of the $SnN_x$ films with different deposition temperature ($T_S$). Intrinsic

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point defects, grain boundaries and thermal decomposition play a vital role in tuning the FM and conductivity of the samples.

## 2. Experimental details

Polycrystalline tin nitride ($SnN_x$) films were deposited on Si (100) and quartz substrates in the temperature range from 100 to 550 °C by DC magnetron reactive sputtering of Sn (99.9%) metal target. The base pressure of the chamber was pumped to $3.0 \times 10^{-5}$ Pa and then a mixture gas of Ar (99.999%) and $N_2$ (99.999%) was introduced into the chamber. The flow rates of Ar and $N_2$ were adjusted to 30 sccm and 50 sccm with a maintained pressure of 1.0 Pa during deposition. The film thickness was determined by a Dektak 6M surface profiler. The structure and chemical states were measured using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The surface morphology characteristics of the films were examined by means of atomic force microscopy (AFM). The optical transmittance was measured by the UV–vis–IR spectrophotometer. The electrical transport properties were measured by physical property measurement system (PPMS) at temperatures ranging from 5 K to 305 K. Magnetization measurements were carried out using Quantum Design magnetic property measurement system (SQUID). The samples on the quartz substrates are only used for the investigation of optical properties and other measurements are all performed on the samples of Si substrates.

## 3. Results and discussion

Fig. 1 gives the XRD patterns for $SnN_x$ films grown on Si (100) substrates at various $T_S$. The film thickness increases from 100 to 120 nm with the $T_S$ due to the improvement of tin atom mobility and their reactivity with nitrogen. All the diffraction peaks can be well indexed to the hexagonal structure of $SnN_x$ with a preferred orientation along [101] except for the film deposited at 100 °C which is amorphous [7]. Inset (a) also shows the XRD pattern of $SnN_x$ film fabricated on quartz substrate at 450 °C for representation. Except for the amorphous wave packet around 23°, the structure characteristics are similar with that on Si (100), indicating that the sample properties are independent to the type of substrate. As the $T_S$ increases the grain size and crystallinity of the films understandably improve, as evidenced by the increase in sharpness and intensity of the XRD peaks. The size of the crystallites oriented along the (101) plane is found to increase from 23 to 37 nm with the $T_S$ calculated by using Scherrer's formula (inset (b) of Fig. 1). Nevertheless, the $SnN_x$ compound is not stable and dissociates into β-Sn when $T_S \geqslant 500$ °C. Along with the precipitated phase, the peaks position shift to lower angle indicating that some exploded Sn atoms may also occupy the interstitial sites,

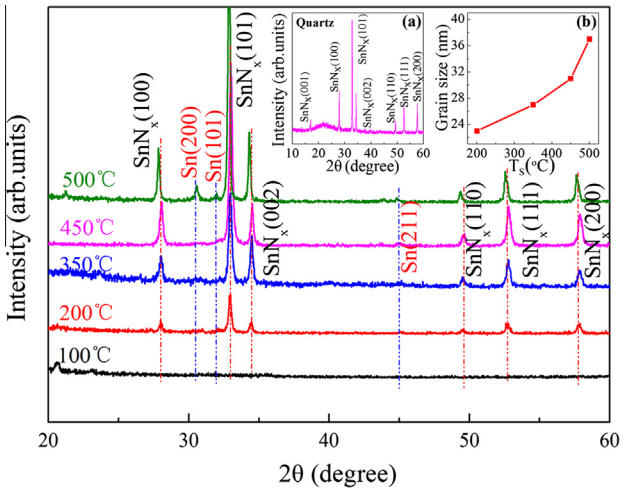


**Fig. 1.** XRD patterns of the polycrystalline $SnN_x$ films fabricated on Si (100) substrates with various substrate temperatures. The inset (a) is the XRD pattern of the polycrystalline $SnN_x$ film fabricated on quartz substrate at 450 °C. (b) Shows the average crystallite size vs. $T_S$.

which leads to the expansion of the lattice. No other impurities such as $SnO_2$ and $Sn_2O_3$ are detected within the instrumental resolution, indicating the samples are of high purity. Furthermore, the lattice parameters of the films (200 °C $\leqslant T_S \leqslant$ 450 °C) are approximative and calculated to be $a$ = 3.6691 Å and $c$ = 5.1972 Å, which are slightly shorter than that of sputtered $SnN_x$ reported by Lima et al. in 1991 ($a$ = 3.723 Å and $c$ = 5.210 Å) [7]. This result suggests that the films prepared in our experiment also have the tin-rich composition with complex defects. For a further investigation, we characterize the surface morphology and measure the grain size and surface roughness of our samples by AFM. In Fig. 2(a–g), one can find significant changes of surface morphology as $T_S$ varies from 100 to 550 °C, reflecting the transition of crystallization quality. The root-mean-square (RMS) roughness of all the films are plotted in Fig. 2(h) and we can get the same changing process between RMS roughness and grain size. It is clearly observed that the surface roughness slightly increases as $T_S$ varies from 100 to 450 °C, and then sharply enlarges. It is similar to the variation of grain size growth, as observed in XRD measurements. When $T_S$ varies from 100 to 450 °C, it increases slightly from 23 to 31 nm, but enlarges by a large margin to 37 nm when $T_S$ further increases 50 °C. This is ascribe to the exploded Sn due to thermal decomposition. They can separate out from the surface and make the RMS roughness substantial increase (Fig. 2(f) and (g)).

Generally, tin-nitride films prepared by reactive magnetron sputtering tend to tin-rich composition with complex defects such as interstitial defect ($Sn_i$) and $V_N$. If there are a large amount of donor defects, the conduction band minimum (CBM) will be filled by the created electrons, making an expansion of band-gap due to the Burstein–Moss (B–M) shift effect [19]. Fig. 3(a) shows the optical transmittance spectra of the films deposited on quartz at different $T_S$. Deducting the influence of the substrate, the transmittance in the visible region is in the range 45–55%. When $T_S \geqslant 500$ °C the fast decomposition of $SnN_x$ leads to nonuniform distribution of the compositions and low visible transmittance of the films ~30%. Fig. 3(b) displays the typical plot of $(\alpha h\nu)^2$ vs. incident energy of the $SnN_x$ films at $T_S$ = 450 °C. The band-gap is approximate 3.10 eV obtained by extrapolating the linear portion to the abscissa and has no significant change with the variation of $T_S$, which is larger than that in the previous report of $SnN_x$ nanowires (~2.9 eV) [20] due to the existence of numerous donor defects (Fig. 3(c)). It is independent of deposition conditions, and consequently independent of crystallinity [8]. The XPS measurements of $SnN_x$ films ($T_S$ = 450 °C and 500 °C) are performed and strong N 1$s$ peaks located at 396.5 eV can be clearly seen, as shown in Fig. 3(d). The N 1$s$ binding energy of about 396.5 ± 0.02 eV has been reported previously [21]. The detected N is almost all bound as nitride, such as the N-Sn combination, and without other N component in the sample. The released $N_2$ by decomposition will cause the peak decreasing in the film of $T_S$ = 500 °C. Moreover, the peaks of Sn 3$d$ shift 0.6 eV toward lower binding energy (Fig. 3(e)). From the observed spin–orbit splitting (8.5 eV) and the binding energy positions of the two peaks, it has been concluded the Sn atoms are main in $Sn^{4+}$ state. One possible explanation for this observation might be the tendency that a certain amount of nitride decomposes. The decomposition of $SnN_x$ is significantly suppressed at $T_S \leqslant 450$ °C, but activated when $T_S \geqslant 500$ °C. The precipitated β-Sn with lower binding energy which located at 483.8 eV (Sn $3d_{5/2}$) may lead to this peak shift [21]. As calculated from the XPS spectra of Sn 3$d$ and N 1$s$, the atomic ratio between Sn and N is about 3:2 in the film of $T_S$ = 450 °C and decreases to 3:1 at $T_S$ = 500 °C. This is accessible in the tin-rich system with complex defects of $Sn_i$ and $V_N$ which have also been discussed in XRD and optical properties.

Fig. 4 presents the temperature dependence of the normalized resistivity $\rho(T)/\rho(305\ K)$ of $SnN_x$ films under different $T_S$ to investigate the influence of abundant defects on transport property. The