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Atmospheric pressure chemical vapor deposition of tin nitride thin films using a halide source

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Preparation of SnN_x films has been studied by atmospheric pressure chemical vapor deposition using $SnCl_2$ and NH_3 as starting materials. The films were deposited onto a quartz substrate at 550–675 °C with growth rates of 0.1–2.5 μm h^{-1}. They showed a typical X-ray diffraction pattern for SnN_x with a hexagonal structure. The band-gap was estimated to be 2.05 eV from the transmission spectra. The electron probe X-ray microanalysis showed that the N/Sn ratio of the as-deposited films was 0.73–1.10, which was dependent upon the growth temperature. They were conductive with resistivities of 0.3–10 Ω cm. The electrochromism was observed when ±1.0 V (SCE) potentials were applied to the SnN_x films in a 1.0 M Na_2SO_4 electrolyte solution.

1 Introduction

Recently, metal nitride materials have been attracting great interest from the viewpoint of their application to optical devices as well as electronic devices because they have appropriately wide band-gap characteristics. Among these, tin nitride is one of the IV–V compounds and has been scarcely studied. Only two reports were found in very early literature.[1,2] They were both concerned with the synthesis of bulk tin nitride from $SnCl_4$ and NH_3 by dc discharge. In 1975, Remy and Hantzpergue first reported the preparation of tin nitride thin films by reactive cathodic sputtering.[3,4] In 1987, the patent for the synthesis of conductive tin nitride films using $SnCl_4$ and NH_3 was issued.[5] However, little about the preparation of crystalline tin nitride in bulk or thin film form was described. In the early 1990s, Hoffman *et al.* prepared tin nitride films by atmospheric pressure chemical vapor deposition (AP-CVD) using $Sn(N(CH_3)_2)_4$ and ammonia[6] although the former chemical is a special and costly compound. Since then, tin nitride films has been prepared by various techniques such as reactive sputtering,[7,8] reactive ion plating,[9] magnetron sputtering[10,11] and plasma-enhanced CVD.[12] However, no one has examined vapor phase deposition of tin nitride films under atmospheric pressure.

We have already reported a new technique, called atmospheric pressure chemical vapor deposition using a halide source (AP-HCVD), for the preparation of the iron nitride thin films.[13–16] From the technological viewpoint, this method has several advantages: (a) Growth of films is feasible by evaporation of simple inorganic compounds such as chlorides, bromides and iodides under atmospheric pressure, followed by reaction with ammonia. (b) Such halides are commercially available in high purity. (c) The deposition rate is as high as that of conventional vapor phase deposition but the resulting films are of high quality.

In the present work, therefore, we examine the AP-HCVD of SnN_x on a quartz substrate using tin(II) chloride as a source.

2 Experimental

Thin films of tin nitride were prepared by AP-HCVD. The apparatus used in this study is illustrated in Fig. 1. This system consists of a horizontal hot-wall quartz reactor with two independent lines to supply $SnCl_2$ and NH_3 vapors. The temperature profile of the reactor is also illustrated in Fig. 1. Thin films were deposited onto the quartz substrate in the hot-wall reactor by the reaction of $SnCl_2$ with NH_3 under atmospheric pressure. During the deposition, $SnCl_2$ was evaporated from the source boat at a temperature of 250 °C. The vapor was then supplied to the growth zone. Purified hydrogen was used as a carrier gas. Typical growth conditions are summarized in Table 1.

The crystallographic structure of the deposited thin films was examined by X-ray diffractometry (XRD) using a Geigerflex (Rigakudenki Co.) operated at 30 kV with a filament current of 15 mA and Ni-filtered Cu-Kα radiation. The thickness and surface morphology of the films were observed both by scanning electron microscopy (SEM) using a Superscan (Shimadzu Co.) and by atomic force microscopy (AFM, Shimadzu Co.). Absorption and transmission spectra were recorded on a Varian 2390 spectrophotometer. Chemical composition of the as-grown films was assayed using the samples of 1 mm in diameter by electron probe X-ray

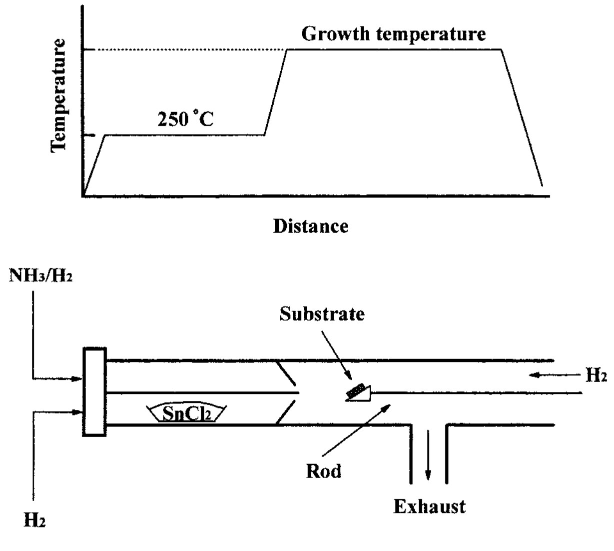

Fig. 1 Schematic diagrams of the apparatus and the temperature profile used in this work.

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Table 1 Typical growth conditions

$SnCl_2$ partial pressure	5.1×10^{-6} atm
NH_3 partial pressure	2.5×10^{-1} atm
$SnCl_2$ source temperature	250 °C
Carrier gas	H_2
Total flow rate	800 cm^3 min^{-1}
Growth temperature	550–700 °C
Duration of deposition	1 h

microanalysis (EPMA, JEOL) with a probe current of 3.8×10^{-8} A and an accelerating voltage of 15 kV. Film resistivities were measured on a Veeco Model FPP-100 instrument by the four-point probe method. Cyclic voltammetry (CV) was employed in order to characterize the electrochromic behavior using the films on indium-tin oxide (ITO)/quartz substrate prepared at 550 °C. A Pyrex cell was used for CV and set in the compartment of a spectrophotometer (JASCO V500). Cyclic voltammogram was measured using a potentiostat (TOHO 2000) with a standard three-electrode configuration consisting of a working electrode for thin films, a Pt counterelectrode and a conventional saturated calomel electrode (SCE) as a reference. 1.0 M Na_2SO_4 was used as an electrolyte.

3 Results and discussion

X-Ray diffraction patterns of the as-deposited films at various growth temperatures are shown in Fig. 2(a)–(d). As is seen from Fig. 2, observed intense peaks are the diffractions assigned to SnN_x independent of the growth temperature. No trace of the peaks for β-Sn and SnO is found. Therefore, it is presumed that the films are composed of SnN_x crystallites with a hexagonal structure and with strong (002) plane texturing. This implies that they have the same structure as those prepared by the sputtering method.[7,8,10,11] The intensity of the diffraction lines increases with increasing growth temperature from 550 to 675 °C. It is therefore evident that the crystallinity is significantly affected by the temperature. The lattice constants a and c of the hexagonal SnN_x film deposited at 675 °C were calculated to be 3.68 and 5.28 Å, respectively. They are slightly shorter than the reported ones of $a = 3.69$ and $c = 5.29$ Å.[7]

Fig. 3 shows the growth rate of the SnN_x film as a function of the growth temperature. As is evident from Fig. 3, the growth rate increases from 0.1 to 2.5 μm h^{-1} with increasing growth temperature from 550 to 675 °C. For the sputtering, which showed the highest growth rate of all those reported earlier, it was about 0.5 μm h^{-1}. Thus, the growth rate in this study is 50 times higher than that for sputtering. Therefore, it is apparent that AP-HCVD using the $SnCl_2$–NH_3–H_2 system is of promise for the SnN_x film preparation with a high growth rate.

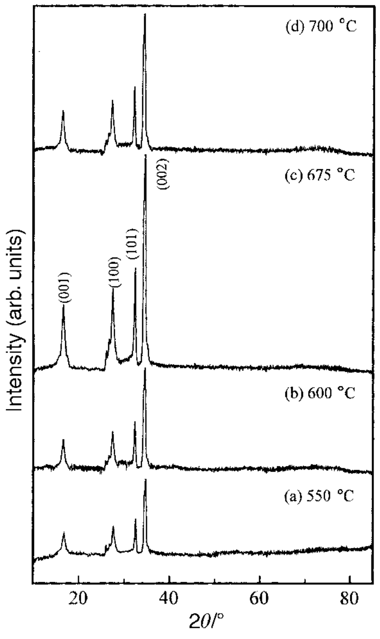

Fig. 2 XRD patterns of the tin nitride films deposited at various growth temperatures.

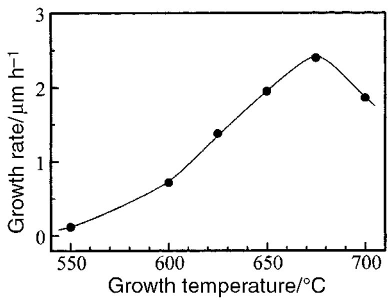

Fig. 3 The growth rate of SnN_x as-deposited films as a function of the growth temperature.

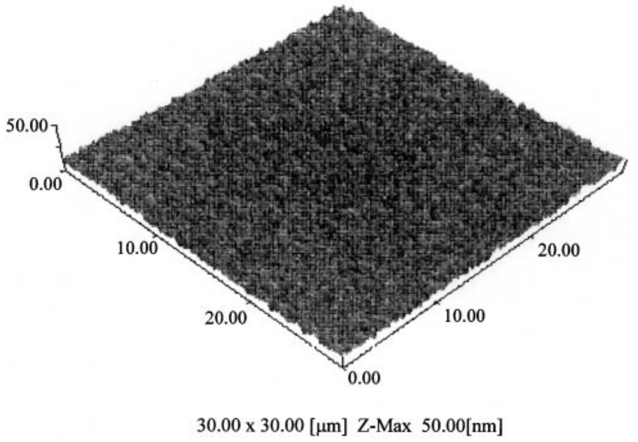

Fig. 4 AFM images of the SnN_x film deposited at 675 °C.

AFM image of the SnN_x film deposited at 675 °C is shown in Fig. 4 together with the corresponding surface roughness. The mean square roughness in a 30×30 μm^2 of the SnN_x film was less than 0.4 nm. It is worth noting that the surface morphology of the SnN_x film is smooth despite the fact that the growth rate is high. All of the SnN_x films prepared in this study also showed similar morphology.

The absorption spectrum of the SnN_x film is shown in Fig. 5. A gradual increase of the absorbance is observed as the wavelength is increased. Therefore, the film of SnN_x is light brown. Optical band-gaps for the films were estimated to be 2.05 eV from transmission spectra by plotting $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$, where α is the absorption coefficient and $h\nu$ the photon energy.

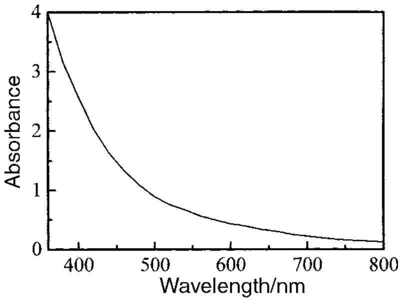

Fig. 5 Adsorption spectrum for a SnN_x film deposited on quartz substrate at 675 °C.

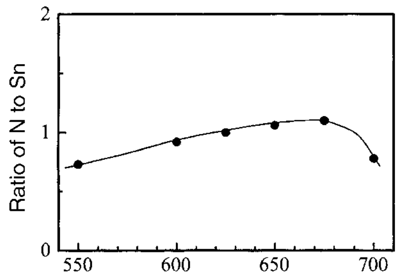

Fig. 6 Atomic ratio of nitrogen to tin in the film as a function of the growth temperature.

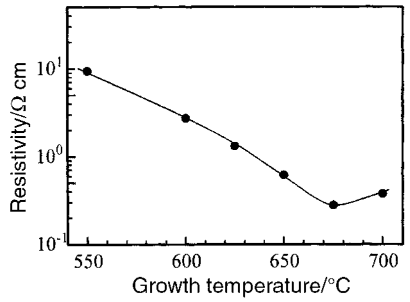

Fig. 7 Electrical resistivity of the SnN$_x$ film as a function of the growth temperature.

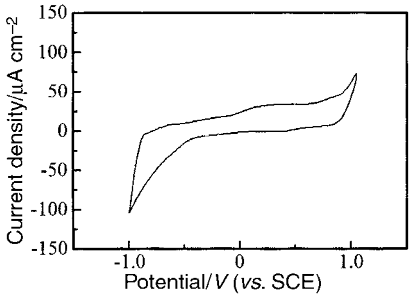

Fig. 8 Cyclic voltammogram of the SnN$_x$ film deposited on an ITO/quartz substrate at 550 °C.

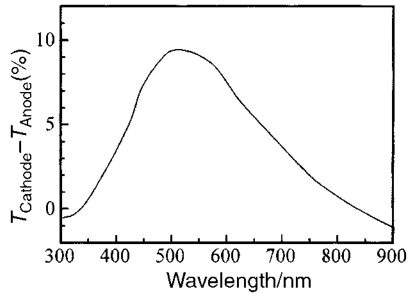

Fig. 9 Difference in transmittance of the SnN$_x$ film under cathodic (−1.0 V) and anodic (+1.0 V) potentials.

The composition of the SnN$_x$ films were measured by means of EPMA, in which oxygen and chlorine were not detected in any of the films. Fig. 6 shows the atomic ratio of nitrogen to tin (N/Sn) as a function of the growth temperature. The N/Sn ratio increases from 0.73 to 1.10 as the growth temperature is increased from 550 to 675 °C. In contrast, at a higher growth temperature of 700 °C the ratio decreases to 0.75. Therefore it is deduced that the re-evaporation of atomic nitrogen occurs from the SnN$_x$ films at temperatures above 675 °C.

Fig. 7 shows the resistivity of SnN$_x$ films as a function of the growth temperature. It is obvious that the resistivity decreases with increasing growth temperature up to 675 °C. It was 0.3 Ω cm at 675 °C. A comparison of the results in Figs. 2 and 7 suggests that the decrease of resistivity is attributable to the improvement in crystallinity of the SnN$_x$ film. Also, it is noteworthy that the obtained value is significantly lower than that for the sputtered films (1.43–66.7 Ω cm).

Fig. 8 shows the cyclic voltammogram of the SnN$_x$ film on an ITO/quartz substrate prepared at 550 °C. It is clear that the film is reduced at a potential of −0.6 V (SCE), and oxidized at a potential of +0.7 V (SCE). Fig. 9 shows the difference between the transmittances of the SnN$_x$ film under cathodic (−1.0 V) and anodic (+1.0 V) potentials. It reveals a maximum difference of 10% in the vicinity of 520 nm, which confirms that noticeable electrochromism occurs for the SnN$_x$ films obtained in this work.

4 Conclusion

Thin films of tin nitride (SnN$_x$) were successfully deposited onto both quartz and ITO/quartz substrates by AP-HCVD. The X-ray diffraction showed a characteristic pattern of the hexagonal SnN$_x$ phase, and the maximum growth rate was approximately 2.5 μm h^{-1} at 675 °C. The bandgap of the SnN$_x$ film was calculated to be 2.05 eV from the transmission spectrum. The N/Sn ratio was in the range of 0.73–1.10, which was dependent upon the growth temperature. The films were conductive and have resistivities of 0.3–10 Ω cm. The electrochromic behavior, which reveals a maximum difference in transmittance of 10% at 520 nm, was observed in the 1 M Na_2SO_4 electrolyte solution.

Acknowledgements

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