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Single-source MOCVD of binary alloy CoSn thin films

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Polycrystalline CoSn alloy thin films have been successfully prepared by low-pressure chemical vapor deposition from two single-source organometallic precursors containing Co–Sn bonds, $Me_3SnCo(CO)_4$ at 250–300 °C and $Ph_3SnCo(CO)_4$ at 300–400 °C. Deposition rates were 250–660 Å min^{-1}. Deposited films were characterized by scanning electron microscopic, energy dispersive spectroscopic, atomic absorption spectroscopic, X-ray diffraction, and Auger electron spectroscopic analyses. Co and Sn elements are evenly distributed in the films. The films are composed of the CoSn phase with a minor constituent of α-Co_3Sn_2.

Introduction

The chemical vapor deposition of binary metal alloy or mixed-metal oxide thin films from single-source precursor has attracted much research interest due to the fact that this approach has the potential to control the film stoichiometry, to simplify the precursor delivery, and to gain better film homogeneity.[1] This strategy has been successfully employed to produce the III–V semiconductor thin films.[2] However, relatively few examples of metal alloy thin films deposited by this method are known. Czekaj and Geoffroy[3] reported the preparation of Fe/Co alloy and oxide films from Fe–Co carbonyl clusters. Liu *et al.*[4] have prepared Fe–Co and Fe–Ni thin films from the corresponding heterobinuclear metal carbonyl compounds by low-temperature photochemical vapor deposition. Shore *et al.*[5] recently reported the CVD of $FeCo_3$ and $FeRu_3$ alloy films from $HFeCo_3(CO)_{12}$ and $HFeRu_3(CO)_{13}$, respectively. Kaesz[6] and Fischer[7] and their co-workers have used a variety of organometallic compounds containing transition metal–Group 13 metal bonds to deposit the corresponding metal alloy thin films. Aylett's group has used silyl transition metal carbonyl compounds to deposit metal silicide films such as CoSi, β-$FeSi_2$, Mn_5Si_3.[8] Transition metal/tin alloys which are generally manufactured by electrodeposition, are known to be useful for anti-corrosion protection, solar energy devices and magnetic tape.[9] Doppelt and Baum[10] reported the deposition of the Sn-doped copper thin films from (β-diketonato)copper complexes of vinyltrimethyltin and vinyltriethyltin. In this paper, we present the use of two organometallic compounds containing Co–Sn bonds, $R_3SnCo(CO)_4$ (R = Me and Ph), as precursors to deposit thin films of binary CoSn alloy.

Experimental

Precursor preparation

All operations were carried out using standard vacuum-line techniques or in a glove box under N_2. Two organometallic precursors, $Me_3SnCo(CO)_4$ and $Ph_3SnCo(CO)_4$, were synthesized by the methods described in the literature[11] and were purified by sublimation under reduced pressure (*ca.* 0.1 Torr). These compounds were characterized by elemental analyses,[12] IR (Perkin-Elmer Model 16 PC FTIR) and mass (VG Trio 2000) spectroscopic methods.

Substrate preparation

Substrates of two types, Si(100) wafer and Si wafer coated with 2000 Å of thermally grown SiO_2, were used. The substrates, typically 1.5×1.5 cm^2, were cleaned with deionized water, acetone and 1,1,1-trichloroethane and then heated to 100 °C for 20 min before use.

Chemical vapor deposition apparatus and procedure

The low-pressure CVD experiments were carried out in a cold-wall, lamp-heated, turbomolecular-pumped reactor (Fig. 1). The precursor (approximately 0.5 g) was loaded into the precursor reservoir in a nitrogen glove box. After loading the reactor with a substrate and connecting the precursor reservoir, the system was evacuated to a base pressure of 8×10^{-6} Torr. The precursor was then heated to an appropriate temperature [40 °C for $Me_3SnCo(CO)_4$ and 90 °C for $Ph_3SnCo(CO)_4$] and was sublimed into the reaction chamber without any carrier gas. The system pressure was kept constant (*ca.* 5×10^{-2} Torr) by adjusting the pumping speed. The substrate was heated from the rear by a mercury lamp and the temperature was measured by a thermocouple touching the front of the substrate.

Film characterization

Deposited films were characterized by scanning electron microscopy (SEM, JEOL JSM-5400), X-ray diffraction (XRD, MAC Science MXP18), Auger electron spectroscopy (AES, Fison Microlab 310D), energy dispersive spectroscopy (EDS, Link Analytical ZAF4/FLS), and atomic absorption spectroscopy (AAS, Perkin-Elmer 3110). Film resistivities were measured with a four-point probe.

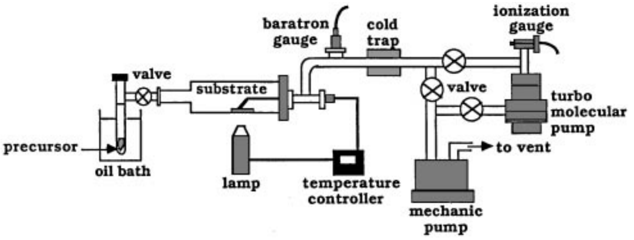

Fig. 1 Schematic plot of cold-wall CVD reactor.

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Table 1 Precursor, growth condition and results of MOCVD of CoSn thin films

				Co/Sn ratio	
Precursor	T_{dep}/°C	Film color	XRD	EDS	AAS
$Me_3SnCo(CO)_4$	250	gray-black	CoSn	1.11	1.22
	300	gray-black	CoSn	1.02	1.14
$Ph_3SnCo(CO)_4$	300	gray	$CoSn/Co_3Sn_2$	1.01	1.07
	350	gray	$CoSn/Co_3Sn_2$	1.07	1.15
	400	gray	$CoSn/Co_3Sn_2$	1.10	1.21

Results and discussion

Deposition were undertaken over the temperature range 250–300 °C and 300–400 °C for $Me_3SnCo(CO)_4$ and $Ph_3SnCo(CO)_4$, respectively. The experimental results are summarized in Table 1. Dense, uniform thin films, gray to black in color, were grown on both Si and SiO_2-coated substrates in these experiments. All films had good adhesion according to the Scotch tape test. Deposition rates were 250–660 Å min^{-1} and increased with increasing the deposition temperature. Film resisitivities range from 12 to 25 μΩ cm.

The surface morphologies of the films were examined by scanning electron microscopy; a typical example deposited from $Me_3SnCo(CO)_4$ on a Si substrate at 300 °C is shown in Fig. 2. The grain size increased with increasing deposition temperature and ranges from 0.2 to 1 μm. Electron probe microanalysis (EPMA) indicated that Co and Sn were evenly distributed in the films. The SEM and EPMA micrographs of the film deposited from $Ph_3SnCo(CO)_4$ at 300 °C are shown in Fig. 3.

X-Ray diffraction analyses of these films show the existence of polycrystalline materials. Diffraction patterns of the films prepared from $Me_3SnCo(CO)_4$ correspond to the single-phased CoSn alloy[13a] and an XRD spectrum of a sample deposited on Si at 300 °C is shown in Fig. 4(top). The patterns of the films deposited from $Ph_3SnCo(CO)_4$ showed the CoSn phase with a minor constituent of α-Co_3Sn_2[13b] [see Fig. 4 (bottom)]. These results are consistent with other surface analysis data. Auger electron spectroscopic, energy dispersive spectroscopic, and atomic absorption spectroscopic analyses (see Table 1) demonstrate that Co/Sn ratios in the films are slightly greater than unity. An Auger electron spectrum of a sample prepared from $Ph_3SnCo(CO)_4$ at 300 °C, shown in Fig. 5, reveals that a nearly 1 : 1 Co/Sn ratio exists in the film. High carbon and oxygen impurities probably resulted from surface contamination, since the spectrum was taken without sputtering the surface. These data suggest that the major component of the films is the CoSn phase with a small amount of the α-Co_3Sn_2 phase. Both CoSn and α-Co_3Sn_2 are stable in the atomic range of cobalt between 50 and 58% at reaction temperatures.[14] Thus, the formation of

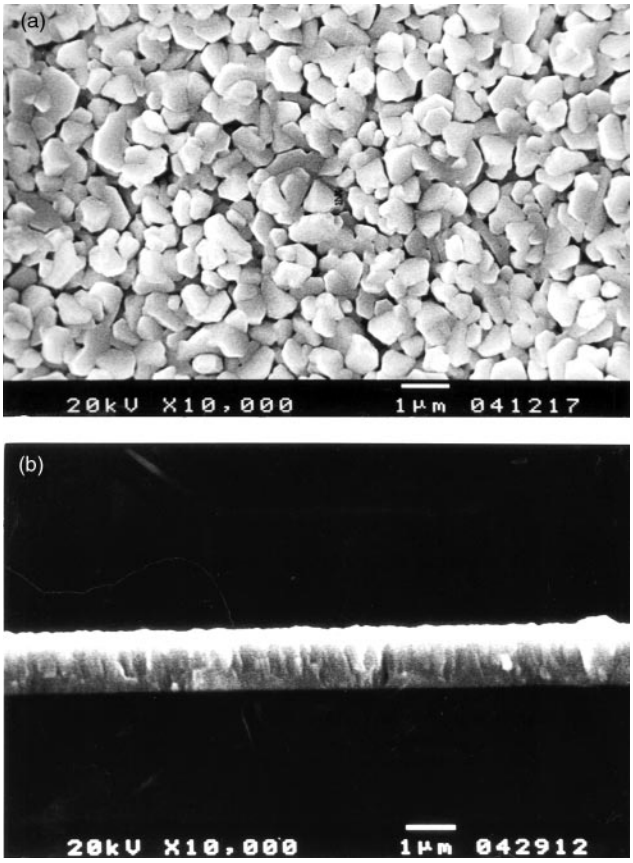

Fig. 2 Scanning electron micrographs of the films deposited from $Me_3SnCo(CO)_4$ at 300 °C: (a) top view, (b) cross-section.

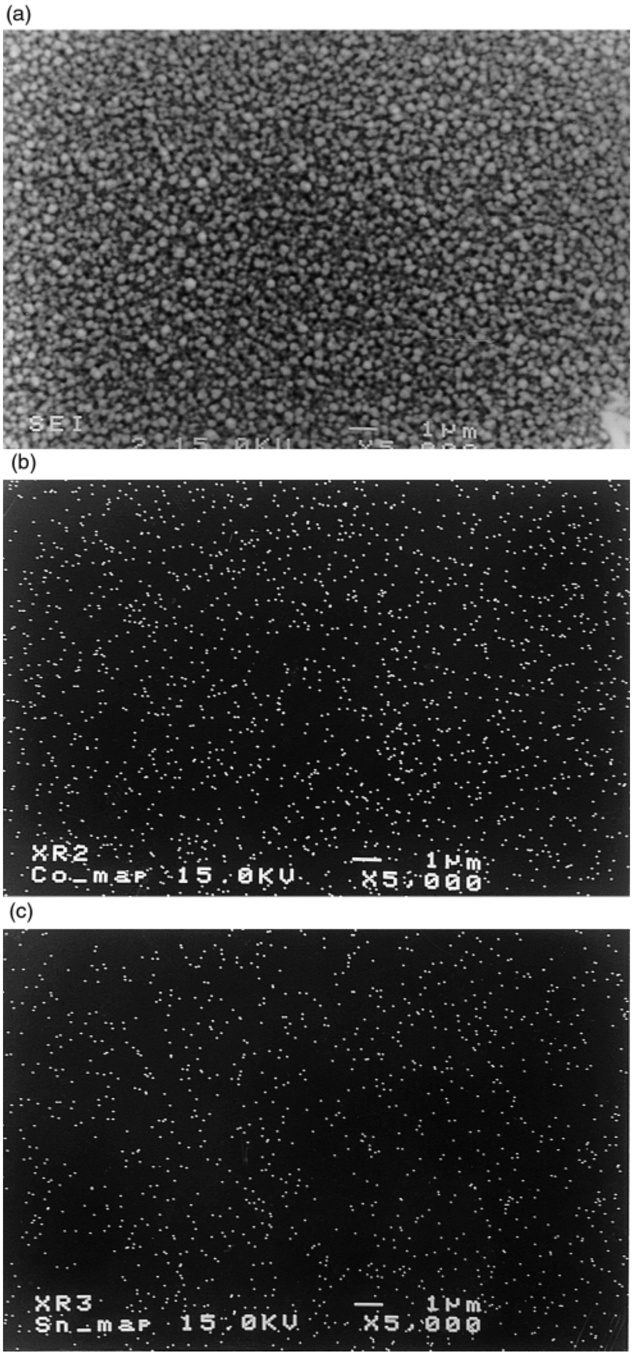

Fig. 3 (a) SEM and EPMA pictures [(b) cobalt, (c) tin] of the film deposited from $Ph_3SnCo(CO)_4$ at 300 °C.

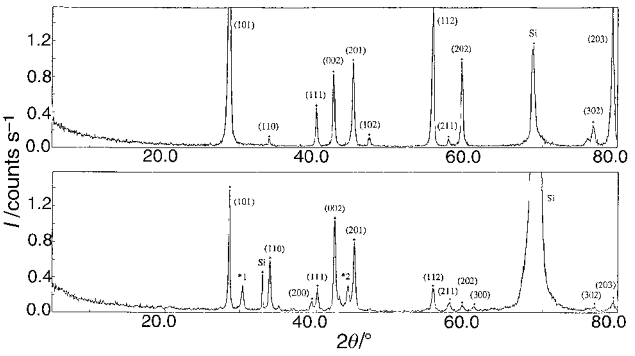

Fig. 4 XRD pattern of the film deposited from (top) $Me_3SnCo(CO)_4$ and (bottom) $Ph_3SnCo(CO)_4$ at 300 °C. [*1, Co_3Sn_2 (101), *2, Co_3Sn_2 (110)].

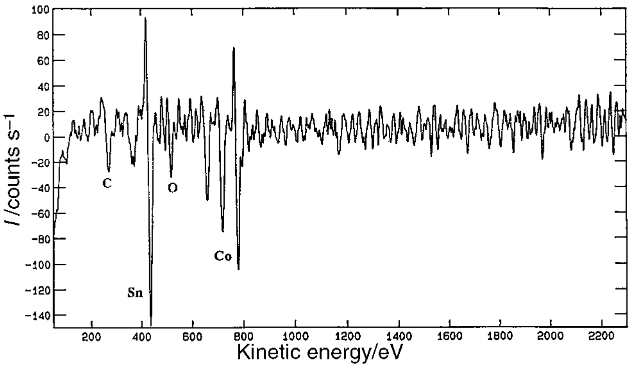

Fig. 5 Auger electron spectrum for the film deposited from $Ph_3SnCo(CO)_4$ at 300 °C. The following elemental composition (atom%) was calculated from this spectrum: Co 46.8%, Sn 43.5%, O 5.6%, and C 4.1%.

the products seems to be thermodynamically controlled. Hot-wall CVD experiments have also been conducted, however, they provided amorphous films with random Co/Sn compositions. These are probably due to the decomposition of precursors prior to their reaching the substrates.

Conclusion

Polycrystalline CoSn alloy thin films have been successfully deposited from two single-source organometallic precursors $R_3SnCo(CO)_4$ (R = Me and Ph). The films are composed of a CoSn phase with a minor constituent of α-Co_3Sn_2. These results are encouraging for further development of hetero-bimetallic, single-source precursors to deposit binary alloy thin films.

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12 Elemental analysis data: for $Me_3SnCo(CO)_4$, calc. C, 25.11%, H, 2.71%; found C, 25.40%, H, 2.78%. For $Ph_3SnCo(CO)_4$, calc. C, 50.72%, H, 2.90%; found C, 51.03%, H, 2.86%.

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