Transition Metal Sulfide Thin Layers Using Dithiocarbamate Complexes by Single-source MOCVD Technique; Cobalt and Nickel Sulfide Thin Layers

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Cobalt and nickel sulfide thin layers were successfully prepared by single-source MOCVD technique using $Co(S_2CNEt_2)_3$ and $Ni(S_2CNEt_2)_2$ respectively. Cobalt sulfide thin layers grown at T_{growth} of 723 K were cubic cobaltpentlandite (Co_9S_8) phase. The surface resistivity and the magnetic susceptibility were $1.06-2.06 \times 10^2$ Ωcm at 298 K and $1.85-2.67 \times 10^5$ emu/ mol at 77.5 -175.5 K. Hexagonal heazlewoodite (Ni_3S_2) phase was grown at T_{growth} of 773 K from $Ni(S_2CNEt_2)_2$, and the growth rate of Ni_3S_2 layer was estimated as 0.18 μm ·h^{-1}. Moreover, the optical band gap was estimated as 0.24 eV, being coincided to that of bulk $NiS_{1.03}$.
Key words: Metal sulfides, Cobalt sulfide, Nickel sulfide, Single-source precursor, MOCVD

1.INTRODUCTION

Transition metal sulfides are potentially applicable to wide variety of fields [1]. Hence, it is necessary to develop a new technique to grow layers of transition metal sulfides. Various experimental techniques have been employed in growth of thin layers of transition metal sulfide such as sputtering, MOCVD (Metal Organic Chemical Vapor Deposition) [2-11], plasma CVD and CBD (Chemical Bath Deposition)[2, 3]. We have already proposed that some transition metal sulfide thin layers were successfully prepared through MOCVD technique using the corresponding transition metal dithiocarbamate complexes as a single-source precursor [4-9]. For example, homogeneous β-ZnS [5] and $Cu_{1.8}S$ [6] layers can be grown on Si(111) substrates using $Zn(S_2CNEt_2)_2$ and $Cu(S_2CNEt_2)_2$, respectively. In this paper, we will describe that growth of cobalt sulfide and nickel sulfide thin layers expecting for the uses as magnetic materials [1] and narrow gap semiconductors [16-23], respectively.

2. EXPERIMENTAL

2.1 Preparation

2.1.1 Preparation of tris(N,N-diethyldithiocarbamato)cobalt

$CoCl_2 \cdot 6H_2O$ (30 mmol) was dissolved in CH_3CN (450 cm^3) under N_2 for 2 h. Then $HN(C_2H_5)_2$ (150 mmol) was added dropwised to the suspension and further stirred at room temperature for 1 h. Successively, CS_2 (90 mol) was added dropwised to the system with cooling for 2 h, then the mixture was heated at 353 K for 20 h. After the reaction, precipitates were filtered off and were dried *in vacuo*. Collected precipitates were recrystallized from CH_3CN several times [yield after a

recrystallization, 90%], which were employed as precursor. Tris(N,N-diethyldithio-carbamato)cobalt was identified by melting point, IR spectra, ^1H- and ^{13}C-NMR(CDCl$_3$) and X-ray crystal structure analysis. Selected crystal data of $Co(S_2CNEt_2)_3$ were summarized in Table 1 and its crystal structure was illustrated in Fig. 1. $Co(S_2CNEt_2)_3$; mp 543.65-544.15 K, IR 1492 cm^{-1}(νC-N), 1001 cm^{-1}(νC=S), ^1H-NMR(CDCl$_3$) δ 1.3(CH$_3$, 18H, t), 3.6(CH$_2$, 6H, q), 3.8(CH$_2$, 6H, q), ^{13}C-NMR(CDCl$_3$) δ 12.5(CH$_3$), 42.7(CH$_2$), 204.6(C=S).

Table 1   Selected crystal data of $Co(S_2CNEt_2)_3$.

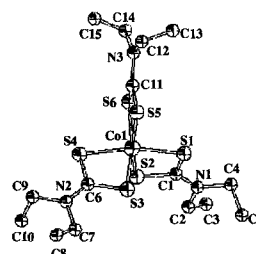| Formula	$C_{15}H_{30}N_3S_6Co$
Formula weight	503.72
Crystal system	Monoclinic
Space group	C2/ c (# 15)
a/ Å	14.0970(9)
b/ Å	10.2968(8)
c/ Å	17.049(1)
β/ °	110.142(5)
V/ Å^3	2323.3(3)
D/ g·cm^3	1.800
Z	5
R, Rw	0.073; 0.063

Fig. 1 X-ray single-crystal structure of $Co(S_2CNEt_2)_3$.

2.1.2 Preparation of bis(N,N-diethyldithiocarbamato)nickel

Bis(N,N-diethyldithiocarbamato)nickel was synthesized from NiO by the method as previously reported [4].

2.2 Characterization

IR spectra were recorded on a Nicolet 5ZDX FT spectrometer with KBr pellets. ^{1}H and ^{13}C NMR were recorded using a Varian UNITY 300 FT-NMR (7.05 T). Crystal structure of Co($S_2CNEt_2)_3$ was solved by Rigaku AFC-7 four axis single crystal diffractometer. Layer crystallinity was assessed with a Rigaku RINT2200L X-ray diffractometer operated at Cu-Kα, 40 kv/40 mA (XRD). Samples were mounted horizontally, and scanned from 20-80 ° in steps of 0.02 °, with account time of 2 θ. Scanning electron microscopy (SEM) studies were done with a JEOL JSM-840 microscope operating at an acceleration voltage of 15 eV.

Magnetic susceptibility of cobalt sulfide specimen was measured by a Shimadzu magnetic balance (Type: MB-11, No, 43921) in the current of 9.0 A. Surface morphology studies of layers were performed on a Shimadzu SPM-9500J scanning probe microscopy (AFM). Measurements were made in dynamic mode; microcantilevers fabricated of Si_3S_4 (OLYMPUS) with spring contact 42 Nm^{-1} and a tip radius of 20 nm and resonant frequency of 300 kHz were used. Optical bandgap measurements were carried out using samples deposited on a quartz substrate.

2.3 MOCVD Setup and Growth Procedure

Growth experiments were carried out in a hot-walled horizontal MOCVD setup[4]. Substrates loaded on a pedestal were initially placed in the quartz tube, and a bubbler attached to the tube. The angle of the substrate against the stream of precursor was arranged as 60, 90 or 180 ° and the distance of the substrate from the inlet was also altered as 4, 6 or 10 cm. After the whole

Table 2   Typical MOCVD parameters.

	Cobalt sulfide	Nickel sulfide
Precursor	Co($S_2CNEt_2)_3$	Ni($S_2CNEt_2)_2$
N_2 flow rate	30-100 cm^3·min^{-1}	
P_{growth}	60-250 Pa	
T_{growth}	623-773 K	625-823 K
T_{sou}	548 K	525 K
t_{growth}	1-10 h	
Substrate	Si(111), Si(100); 1.5×1.5 cm,	
	Quartz, Quartz crystal; 1.0×1.0 cm	
Camber	Hot-walled horizontal; Φ 89 × 780 mm	

system was evacuated, precursor in the bubbler and substrates were simultaneously heated at the setting temperature. Then a carrier gas (N_2, purity; 99.99 %) flow was started at the rate of
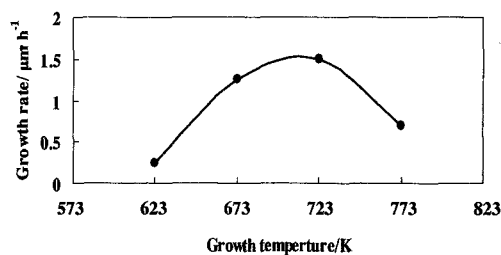
30-100 cm^3·min^{-1}. Typical MOCVD parameters are summarized in Table 2.

3. RESULTS and DISCUSSION

3.1 Growth of Cobalt Sulfide Thin Layers

Thin layers of gray-black appearance were grown at T_{growth} of 623-773 K and their adhesive strength to the substrate seemed to increase with an increase of T_{growth}. Relation of growth rate with temperature is represented in Fig. 2. It is found that the growth rate of cobalt sulfide thin layers increased with an increase of T_{growth} upto 723 K and decreased with temperature. The growth rate at 723 K is largest and was 1.5 μm·h^{-1}.

Fig. 3 shows X-ray diffraction profiles for the samples obtained at T_{growth} of 723 K for t_{growth} of 2 and 6 h together with those of Co_9S_8 cobaltpentlandite (JCPDS#86-2273) and CoS jaipurite (JCPDS#75-0605) reported in the JCPDS files. Both Co_9S_8 and CoS phases were deposited in the samples obtained for 2 h, while only Co_9S_8 phase was detected in the sample for 6 h.

Next the morphology of these layers was observed by SEM images as shown in Fig. 4. It is found that the sample obtained for 2 h displays a rough texture with small crystallites. Prolonged growth period over 2 h should result in an increase of roughness but the size of crystallites increased. It was also seen that growth orientation was random for both t_{growth}.

The relation of surface resistivity with T_{growth} is shown in Fig. 6. Resistivity of the sample grown for 6 h is lower than that for 2 h. Size of the crystallites perhaps influenced larger on the surface resistivity than uniformity. Furthermore, it was obvious that cobalt sulfides obtained at T_{growth} 723 K had a weak magnetic susceptibility which increases with temperature from a value of 1.85 × 10^5 at 77.5 K to 2.67 × 10^5 emu/ mol at 175.5 K. With resapect to the growth rate and adhesion, optimal growth conditions for single phase deposition of cobalt sulfide thin layers were as follows; growth temperature (T_{growth}) 723 K, source temperature(T_s) 548 K, pressure (P_{growth}) 120 Pa, N_2 flow rate 50 cm^3·min^{-1}.

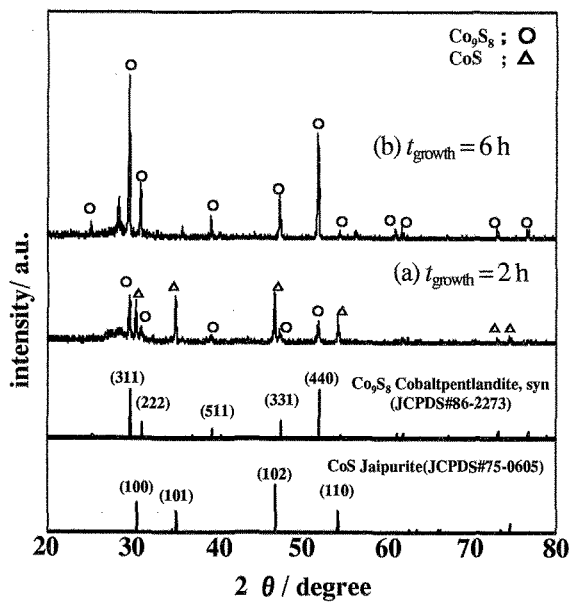**Fig. 2   Relation of growth rate with growth temperature.**

Fig. 3 X-ray diffraction patterns of cobalt sulfide layers grown at 723 K for (a) 2 and (b) 6 h on Si(111).
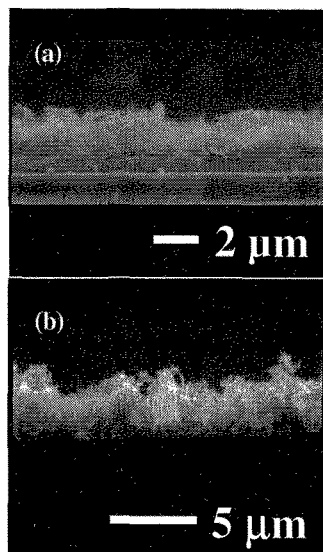

Fig. 4 SEM images of cobalt sulfide layer grown at 723 K for (a) 2 and (b) 6 h on Si(111).
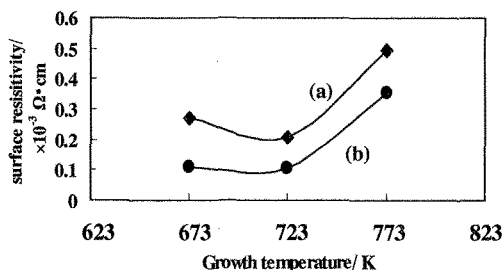

Fig. 5 Surface resistivity of cobalt sulfide layers grown at various temperatures for (a) 2 and (b) 6 h.

3.2 Growth of Nickel Sulfide Thin Layers

We have previously clarified that $NiS_{1.03}$ thin layers could be grown at T_{growth} of 623-673 K on Si(111) substrate [8]. Here, it will be reported that the nickel sulfide thin layers of other phase can be grow at higher temperature region. Now hexagonal Ni_3S_2 heazlewoodite (JCPDS#44-1418) was grown with the preferred growth orientation along (110) direction above T_{growth} of 773 K. This growth direction did not change by altering the substrates such as Si(111), Si(100), and quartz. Thus, it is found that different phases of nickel sulfide layers can be given with altering the growthl temperatures.

Surface and cross-sectional morphologies were observed by SEM images as shown in Fig. 8. Detailed growth conditions were as follows; T_{growth} 773 K, T_{sou} 523 K, P_{growth} 90 Pa, N_2 flow rate 50 $cm^3 \cdot min^{-1}$. The growth of stuffed and homogeneous island crystals were detected and these crystals were grown along 110 plane from the surface of the substrate. Further thickness of Ni_3S_2 thin layers was given as 0.35 μm from the cross section(Fig. 7 d). Then the growth rate of nickel sulfide layers was estimated as 0.18 $μm \cdot h^{-1}$ at 773 K of growth temperature.

The surface morphology which observed by AFM 3D images is shown in Fig. 9. The surface uniformity of Ni_3S_2 layers was superior to that of $NiS_{1.03}$ obtained at below 673 K reported previously [8]. Moreover, the optical band gap, which was measured using the specimen grown on a quartz substrates and estimated by the direct transition method was 0.24 eV, and coincided well to that of bulk crystals of $NiS_{1.03}$ [16-23]. Meanwhile the surface resistivity that is 2.3×10^5 Ω•cm at 298 K is slight higher than that of bulk $NiS_{1.03}$. Further, these layers seemed gold and revealed much stronger adhesive property to the substrates, such as Si(111), Si(100), and quartz. Additionally, it was found that the controling the angle of the substrate against the stream of precursor and the distance of the substrate from the inllet at 60 ° and in 4 cm, respectively, should lead to these results.
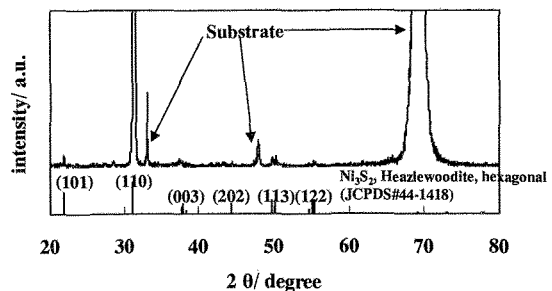

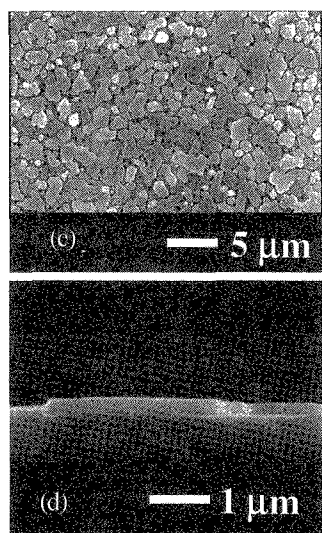**Fig. 6** X-ray diffraction pattern of nickel sulfide layer grown at 773 K for 2 h on Si(100).

Fig. 7 SEM images of nickel sulfide layers grown at 773 K on Si(100) (c) surface and (d) cross-section.
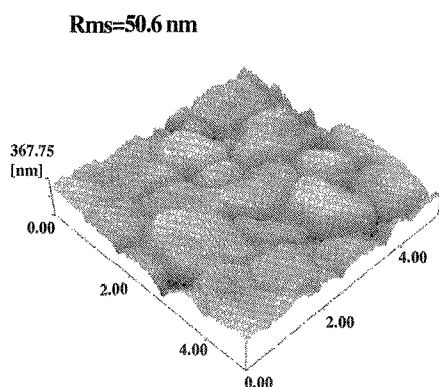
Rms=50.6 nm

Fig. 8 AFM 3D images of nickel sulfide layer obtained at 773 K for 2 h on Si(100).

4. Conclusions

We could obtain Co_9S_8 thin layers in single phase at T_{growth} of 723 K with the single-source MOCVD using $Co(S_2CNEt_2)_3$ as a source. Such Co_9S_8 thin layers possessed relatively weak magneticity. On the other hand, nickel sulfide (Ni_3S_2 phase) thin layers were grown with a preferred orientation along (110) direction on Si(111), Si(100) or quartz at T_{growth} of 773 K. It was found that the band gap of thin layers given at T_{growth} 773 K is 0.24 eV and was somewhat resistive.

5. Acknowledgement

6. References

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