

GROWTH OF TRANSITION METAL SULFIDE THIN FILMS FROM DITHIOCARBAMATE COMPLEXES BY MOCVD TECHNIQUE

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Transition metal sulfide, especially nickel (I) sulfide (NiS) thin films have been successfully prepared using single-source MOCVD technique. Homogeneous NiS thin films were given on Si (111) substrates from single-source precursors, Ni(II)(S₂CNEt₂)₂ under N₂ carrier at substrate temperature of 400 °C. Nickel sulfide thin films obtained were characterized by XRD, SEM and AFM. Electric and semiconductor properties were also reported.

Key words: Transition metal sulfides, nickel sulfide, thin films, MOCVD.

INTRODUCTION

Transition metal sulfides, especially late transition metal analogues, have been attracted much attention over the past few years due to their large potentials for optoelectronic and semiconductor properties¹. We have already proposed that dithiocarbamate complexes were excellent single-source precursor complexes suitable for the growth of such transition metal sulfide thin films. For example, homogeneous β-ZnS and Cu_{1.8}S films can be grown on Si (111) substrates through MOCVD technique using Zn(II)(S₂CNEt₂)₂ or Cu(II)(S₂CNEt₂)₂, respectively^{2,3}. Nickel(II) sulfide is known as one of narrow bandgap semiconductors and potential solar thermal materials⁴⁻⁸. In this paper, we describe the growth of NiS thin film by single-source MOCVD using Ni(II)(S₂CNEt₂)₂.

EXPERIMENTAL

CHARACTERIZATION

IR spectra were recorded on a Nicolet 520X FR-IR spectrometer using KBr pellets. Raman spectra were recorded on a Shimadzu Raman spectrophotometer series 3000. ¹H- and ¹³C-NMR spectra were obtained by a

Varian UNITY 300 FT-NMR (300 MHz). The crystal structure of the Ni complex was solved by Rigaku AFC-7 four axis single crystal diffractometer. X-ray diffraction (XRD) patterns of the thin films of nickel sulfide were recorded on a Rigaku RINT2000L X-ray diffractometer. Scanning electron microscopy (SEM) studies were done with a JEOL JSM-840 microscope operating at 15 kV of acceleration voltage. Surface morphology studies of films were performed on a Shimadzu SPM-9500J scanning probe microscopy (AFM). Measurements were made in contact mode; fabricated Si₃N₄ microcantilevers (Olympus) with a spring constant of 0.15 N m⁻¹ and a tip radius of 20 nm and resonant frequency of 24 kHz were used.

SYNTHESIS OF Ni(II)(S₂CNEt₂)₂⁹

NiO (120 mmol) was suspended in CH₃CN (100mL) under N₂. Then diethylamine, NH(C₂H₅)₂ (240 mmol) and carbon disulfide, CS₂ (240 mmol) were added dropwise to the suspension in this order. Then the mixture was refluxed with stirring for 20 h. The green solid precipitates were filtered off. Collected precipitates were recrystallized from CH₃CN several times. The

dithiocarbamate complex was identified by IR, Raman and ^1H -, ^{13}C -NMR (CDCl_3) spectroscopy. The X-ray crystal structure analysis is represented below. Crystal data were summarized in Table I and the crystal structure was illustrated in Fig. 1. Selected spectral data of $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$ were as following; ^1H -NMR (CDCl_3 , 27.0 °C, 300MHz) δ 1.2 (t, CH_3 , 3H, $J = 7.2$ Hz) 3.6 (q, CH_2 , 2H, $J = 7.2$ Hz); ^{13}C -NMR (CDCl_3 , 27.0 °C, 300MHz) δ 12.4 (CH_3) 43.7 (CH_2) 206.0 ($\text{C}=\text{S}$); IR (KBr) 1524 cm^{-1} ($\text{VC}=\text{N}$), 993 cm^{-1} ($\text{VC}=\text{S}$); Raman 1519 cm^{-1} ($\text{VC}=\text{N}$), 991 cm^{-1} ($\text{VC}=\text{S}$), 423 cm^{-1} ($\text{vNi}-\text{S}$)

Table I Crystal data for $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$

Formula	$\text{C}_{10}\text{H}_{20}\text{N}_2\text{NiS}_4$
Formula weight	355.22
Crystal system	monoclinic
Space group	$\text{P}2_1/c$ (#14)
$a/\text{\AA}$	6.1743(8)
$b/\text{\AA}$	11.5229(8)
$c/\text{\AA}$	11.5978(6)
$\beta/^\circ$	95.797(7)
$V/\text{\AA}^3$	820.9(1)
$D/\text{g cm}^{-3}$	1.437
Z	2
R, Rw	0.079; 0.114

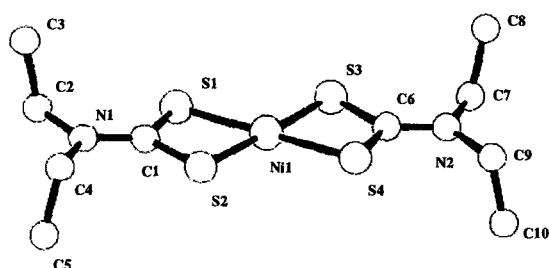


Fig. 1 Crystal structure of $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$.

GROWTH EXPERIMENTS

Growth experiments were carried out in a hot-walled horizontal CVD chamber, shown in Fig. 2. Growth conditions are summarized in Table II. $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$ (0.5 g) was loaded into the bubbler and Si (111)

substrates ($1.5 \times 1.5\text{ cm}^2$) were put onto the pedestal. Then system pressure was held at 120 Pa. Then the chamber and the bubbler were heated to the prescribed temperatures. Then $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$ was transported on N_2 carrier into the chamber.

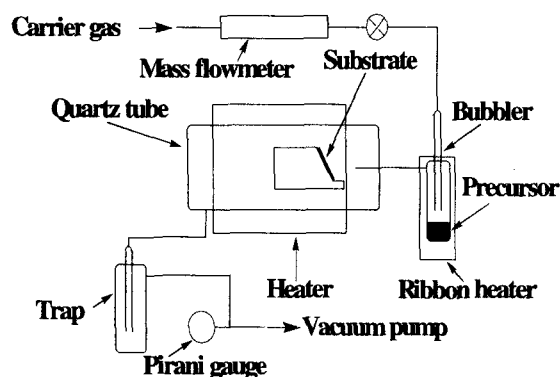


Fig. 2 Experimental MOCVD setup.

Table II Main parameters of the CVD process

parameter	value
chamber	hot-walled horizontal
growth temperature / °C	350–400
source temperature / °C	250
growth periods / h	1–4
pressure / Pa	120
carrier flow rate (N_2) / mL min^{-1}	50

RESULTS AND DISCUSSION

At first, we attempted the static thermal decomposition of nickel bis(*N,N*-diethyldithiocarbamate), $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$, and we found that it could give nickel sulfide, NiS powders quantitatively under inert atmosphere at 400 °C. Additionally, $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$, is monomeric even in solid state as can be seen from Fig. 1 and perhaps possesses considerable vapor pressure applicable to the source for CVD growth of nickel sulfide¹. Consequently it can be said that $\text{Ni}(\text{II})(\text{S}_2\text{CNET}_2)_2$ may be a candidate of an excellent precursor for the growth of NiS through MOCVD process. Growth experiments were done using a horizontal CVD

reactor under reduced pressure (120 Pa) with a fixed source temperature as 250 °C. Below 350 °C of substrate temperature, no film deposition was detected. In contrast, layers of hexagonal NiS_{1.03} phase (JCPDS #2-1273) could be grown on an Si (111) at 350, 375 and 400 °C of substrate temperature.

Scanning electron micrographs (SEM) of the cross-section of NiS films grown at 350 and 400 °C are shown in Fig.3, and they show that the film texture contains fine needles with some leafs and that the direction of growth is random. Typical XRD pattern of the film grown at 400 °C is shown in Fig. 4. Relatively sharp diffraction peaks are detected.

A linear correlation of film thickness with growth periods was obtained at 400 °C as shown in Fig. 5, and the slope indicated that the growth rate is 1.0 μm h⁻¹ at 400 °C.

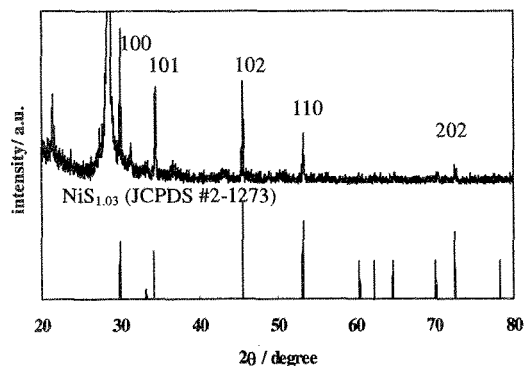
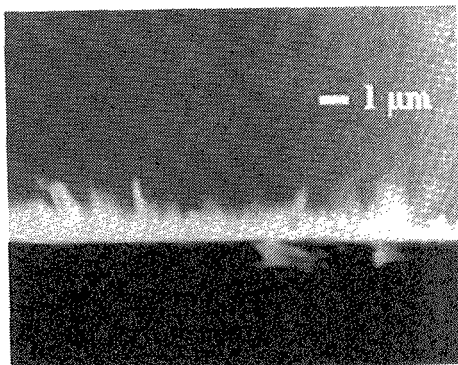


Fig. 4 X-Ray diffraction pattern of NiS_{1.03} film at 400 °C for 2.5 h.

(a)



(b)

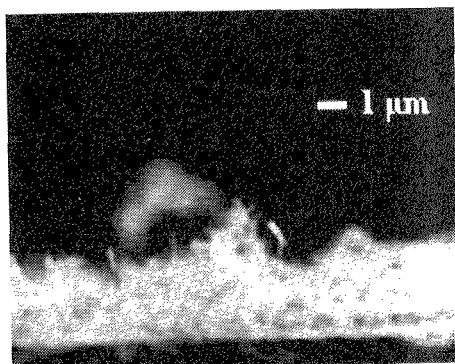


Fig. 3 Scanning electron micrograph images of cross-section of NiS_{1.03} films from Ni(II)(S₂CNEt₂)₂ on Si (111); (a) at 350 °C for 1 h; (b) at 400 °C for 1 h.

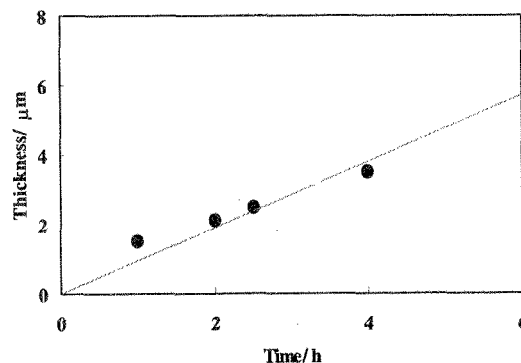


Fig. 5 Time course increase of thickness of NiS_{1.03} films on Si (111) substrates. Growth temperature was 400 °C. (substrate temperature)

Surface morphology was observed with an AFM technique and some 3D images are presented in Fig. 6. Surface roughness of the films decreases with an increase of the growth temperature; thus root mean square (RMS) values for the films grown at 350, 375 and 400 °C are 15.1, 19.4 and 29.4 nm, respectively.

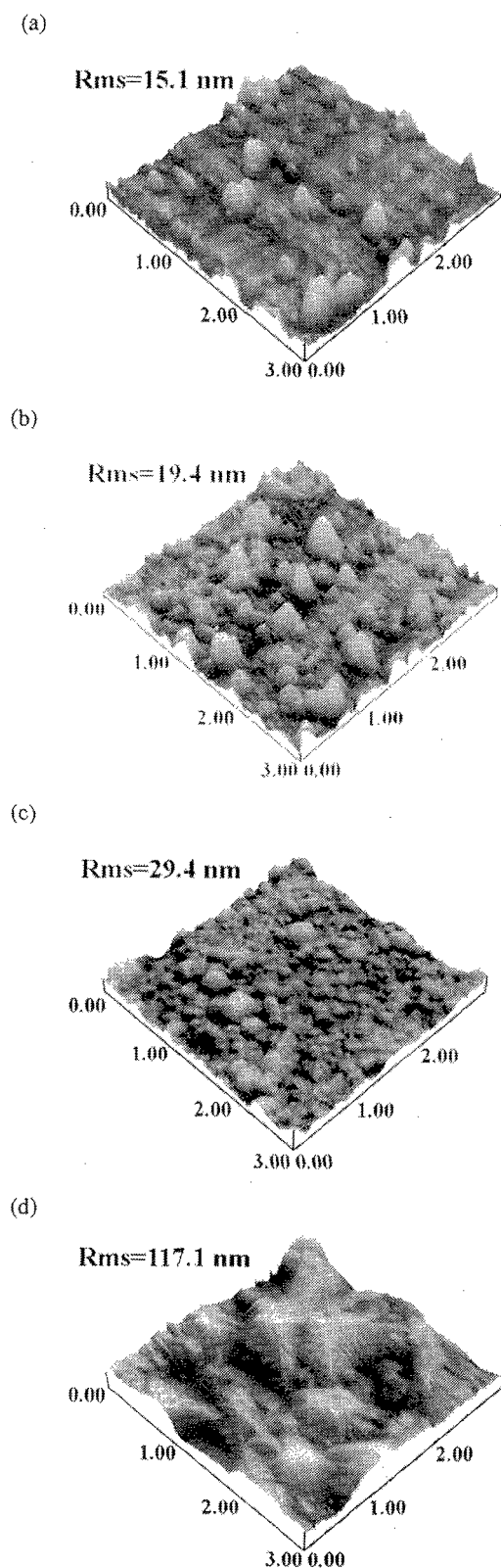


Fig. 6 AFM 3D images of NiS_{1.03} films grown at various temperatures and periods on Si (111) substrates; (a) at 350 °C for 1 h; (b) at 375 °C for 2 h; (c) at 400 °C for 2.5 h; (d) at 400 °C for 4 h.

Additionally, RMS becomes 117 nm by prolonged growth period for 4 h at 400 °C. Consequently we can obtain a homogeneous NiS film at 400 °C of substrate temperature for 4 h (thickness 3.5 μm). An electric conductivity measurement of the homogeneous NiS shows that this film is highly conductive; $8.0 \times 10^4 \Omega \text{ cm}$. Additionally, this film is transparent in IR region and the absorption edge should be placed in near IR region. Optical bandgap energy is then calculated as 0.21 eV from the absorption edge.

CONCLUSION

Homogeneous and conductive NiS thin films (as NiS_{1.03} phase) can be grown by single-source MOCVD using Ni(II)(S₂CNEt₂)₂ at 400 °C. The surface conductivity and optical bandgap energy are $8.0 \times 10^4 \Omega \text{ cm}$, and 0.21 eV, respectively. These values were close to that of NiS film already reported, indicating characteristics of narrow bandgap semiconductor.

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