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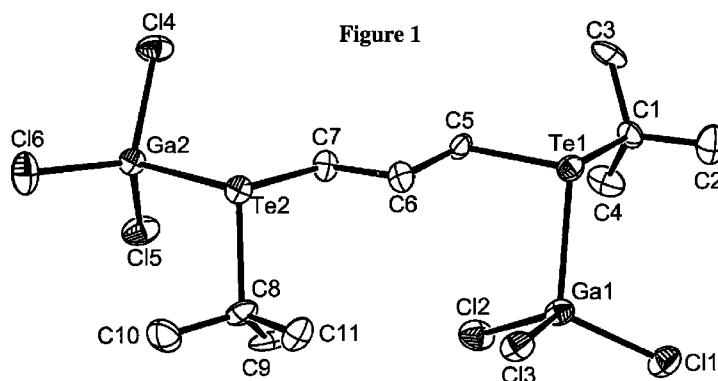
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(54) Title: AN ALKYLTELLUROETHER PRECURSOR FOR USE IN THE SINGLE SOURCE CHEMICAL VAPOUR DEPOSITION OF A METAL TELLURIDE



(57) Abstract: An alkyltelluroether precursor for use in the single source chemical vapour deposition of a metal telluride, which alkyltelluroether precursor comprises an alkyltelluroether ligand bonded to a metal halide, which alkyltelluroether precursor comprises at least one alkyl group containing at least two carbon atoms, and which alkyltelluroether precursor has the general formula: $\text{MX}_n(\text{alkyltelluroether})_y$ where M = metal X = a halide n = 3 or 4, and y = 1, 2 or 3 alkyl = butyl, propyl, ethyl, trimethylsilyl, cyclohexyl, cyclopentyl or benzyl.

AN ALKYLTELLUROETHER PRECURSOR FOR USE IN THE
SINGLE SOURCE CHEMICAL VAPOUR DEPOSITION OF A METAL
TELLURIDE

This invention relates to an alkyltelluroether precursor and, more especially, this invention relates to an alkyltelluroether precursor which is for use in the single source chemical vapour deposition of a metal telluride, and which has at least one alkyl group containing at least two carbon atoms.

There is a significant demand for chemical reagents to produce electronic materials for applications in electronic devices. The production of the electronic devices may advantageously be performed with chemical vapour deposition from the reagent, which ideally is easily handled because it is usually a stable solid, has low toxicity and is not pyrophoric. Often the chemical vapour deposition is not sufficiently selective.

It is an aim of the present invention to reduce the above mentioned problems.

Accordingly, in one non-limiting embodiment of the present invention there is provided an alkyltelluroether precursor for use in the single source chemical vapour deposition of a metal telluride, which alkyltelluroether precursor comprises an alkyltelluroether ligand bonded to a metal halide, which alkyltelluroether precursor comprises at least one alkyl group containing at least two carbon atoms, and which alkyltelluroether precursor has the general formula:



where M = metal

X = a halide

n = 3 or 4, and

y = 1, 2 or 3

alkyl = butyl, propyl, ethyl, trimethylsilyl,

cyclohexyl, cyclopentyl or benzyl.

The alkyltelluroether precursor of the present invention is advantageous in that it enables selective chemical vapour deposition. The alkyltelluroether precursor may be used for the production of electronic devices, with selective deposition being effected onto a patterned substrate with small holes in a very selective manner. Hitherto, chemical vapour deposition would normally lead to deposition everywhere. In contrast, the alkyltelluroether precursor of the present invention enables selective deposition onto certain substrate types, for example only onto the TiN within the shallow holes in lithographically patterned substrates formed of TiN/SiO₂. The alkyltelluroether precursor may further be advantageous in that it is a single source precursor which means that only one entity rather than multiple sources are required. Still further, known compounds that are currently used in chemical vapour deposition in the production of metal tellurides for electronic devices are usually highly unstable, toxic, volatile and flammable. The alkyltelluroether precursor of the present invention avoids or reduces these undesirable properties because it is more stable, less toxic and not pyrophoric.

The alkyltelluroether precursor may be one in which $n = 3$, and in which $M =$ a p-block element. The p-block element may be Ga, In, Al, As, Sb or Bi.

Alternatively, the alkyltelluroether precursor may be one in which $n = 4$, and in which $M =$ a p-block element. The p-block element may be Sn or Ge.

The alkyltelluroether precursor may be one in which $X =$ a chloride or a bromide.

The alkyltelluroether precursor may be one in which the alkyltelluroether is a mono-telluroether TeR_2 , a di-telluroether $\text{RTe}(\text{CH}_2)_n\text{TeR}$ where $n = 1, 3, 4$ or 5 , or a tri-telluroether $\text{MeE}(\text{CH}_2\text{TeR})_3$ where $E = \text{C}$ or Si ; or $\text{RTe}(\text{CH}_2)_3\text{Te}(\text{CH}_2)_3\text{TeR}$, and where R for all of the said alkyltelluroethers = alkyl, cycloalkyl, trimethylsilyl or substituted alkyl. The alkyl may be butyl, propyl, ethyl, trimethylsilyl, cyclohexyl, cyclopentyl or benzyl. The butyl may be n-butyl, t-butyl, or s-butyl. The propyl may be n-propyl or i-propyl. When the alkyltelluroether is a di-telluroether, then it may be for example $\text{EtTe}(\text{CH}_2)_n\text{TeEt}$ where $n = 1, 3$ or 4 .

The alkyltelluroether precursor may be one in which the alkyltelluroether is a di-telluroether and in which the di-telluroether is $\text{BuTe}(\text{CH}_2)_n\text{TeBu}$, where $\text{Bu} =$ n-butyl, t-butyl or s-butyl.

The alkyltelluroether precursor may be one in which the alkyltelluroether is a di-telluroether, and in which the di-telluroether is $\text{PrTe}(\text{CH}_2)_n\text{TePr}$, where $\text{Pr} =$ i-propyl or n-propyl.

The present invention also provides a process of producing a metal telluride using at least one of the alkyltelluroether precursors, which process

comprises of placing the precursor together with a substrate into a chemical vapour deposition apparatus, and heating to a predetermined temperature and pressure until the precursor has evaporated and the metal telluride has been deposited on the substrate.

The process of the invention may be one in which the pre-determined temperature and pressure of 600-900 K, 0.1 mmHg, until the precursor had completely evaporated.

The process of the invention may be one in which the substrate is lithographically patterned TiN/SiO₂ or Si/SiO₂. In such a process the quantity of the single source metal alkyltelluroether precursor may be limited to only deposit onto the desired areas of the substrate and prevent complete coverage of the substrate surface.

The process may be one in which there is only one of the alkyltelluroether precursors. Alternatively, the process may be one in which there are two of the alkyltelluroether precursors.

The process may be one in which the metal telluride is a senide-doped metal telluride, and in which the process comprises using the alkyltelluroether precursor together with the analogous alkylselenoether precursor.

The number of alkyltelluroethers bonded to the metal halide in the reagent may depend upon the choice of metal. For example, for GaCl₃, it will usually be one per metal, while for larger metals, two or even three telluroether ligands may be present. For AlX₃, GaX₃ and AsX₃ usually it will be only one telluroether per MX₃. For InX₃, SbX₃ and BiX₃ there may be 1, 2 or 3 Te ligands per metal depending on how bulky the R groups are on TeR₂.

In order to further illustrate the present invention, reference will now be made to the following Examples which are given for the purposes of illustration only.

For the precursor preparation and characterisation in the Examples 1 - 18 all reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry nitrogen atmosphere. The reagents were stored at -18°C (in a freezer) and manipulated using a glove box. Hexane, toluene, diethyl ether and tetrahydrofuran were dried by distillation over sodium/benzophenone. Dichloromethane was dried over CaH_2 . SnCl_4 , GaCl_3 , BiCl_3 , $n\text{BuLi}$ (1.6 mol dm^{-3} in diethyl ether) and $t\text{BuLi}$ (1.7 mol dm^{-3} in pentane) were obtained from Aldrich and used as received. Te^nBu_2 was prepared by the literature procedure (D. H. O'Brien, N. Dereu, C. K. Huang, K. J. Irgolic and F. F. Knapp Jr., *Organometallics*, 1983, 2, 305-307). IR spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 instrument. Raman spectra on the molecular complexes were obtained using a Perkin-Elmer FT2000R with a Nd:YAG laser. ^1H NMR spectra were recorded from solutions in CD_2Cl_2 on a Bruker AV300, $^{125}\text{Te}\{^1\text{H}\}$, ^{71}Ga , $^{77}\text{Se}\{^1\text{H}\}$ and ^{119}Sn NMR spectra on a Bruker DPX400 and referenced to external neat TeMe_2 , $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ in water, external neat SeMe_2 and SnMe_4 respectively. Microanalytical results were from Medac Ltd. or from London Metropolitan University.

EXAMPLE 1

$n\text{BuTe}(\text{CH}_2)_3\text{Te}^n\text{Bu}$

This is an alkyltelluroether ligand for forming a complex with a metal halide. Freshly ground tellurium powder (8.9 g, 0.07 mol) in dry tetrahydrofuran (140 mL) was frozen in a liquid nitrogen bath. ⁿBuLi (44 mL of 1.6 mol dm⁻³ solution in diethyl ether, 0.07 mol) was added and the mixture allowed to thaw. When all the tellurium had dissolved, the clear solution was refrozen (-196°C) and 1,3-dichloropropane (3.6 mL, 4.28 g, 0.036 mol) added slowly dropwise. The mixture was allowed to warm to room temperature and hydrolyzed with deoxygenated water, followed by separation, extraction with diethyl ether and drying (MgSO₄), under an inert atmosphere. The solvent was removed by distillation and the residue fractionated *in vacuo* to give an air-sensitive red oil. Yield: 8 g, 53%. ¹H NMR (CDCl₃) δ/ppm: 0.91 (t, [6H], CH₃), 1.39 (m, [4H], CH₂), 1.72 (m, [4H], CH₂), 2.13 (m, [2H], 2.68 (m, [8H], CH₂TeCH₂). ¹³C{¹H} NMR (CDCl₃) δ/ppm: 3.85 (CH₂Te, ¹J_{TeC} = 150 Hz), 5.60 (CH₂Te, ¹J_{TeC} = 150 Hz), 14.48 (CH₃), 26.16 (CH₂), 35.42 (CH₂), 35.48 (CH₂). ¹²⁵Te{¹H} NMR (neat) δ/ppm: 289.

EXAMPLE 2

^tBuTe(CH₂)₃Te^tBu

This is an alkyltelluroether ligand for forming a complex with a metal halide. Freshly ground Te (12.76 g, 0.1 mol) was suspended in anhydrous THF (150 mL) and frozen in a liquid N₂ bath. ^tBuLi (63 mL, 0.1 mol) was added and the solution allowed to warm to room temperature with stirring. After 30 minutes a yellow solution formed, which was frozen in a liquid N₂

bath and 1,3-dichloropropane added. The solution was allowed to warm to room temperature with stirring. After 30 minutes the solution had turned brown and a white precipitate had formed. After a further 30 minutes all solvent was removed *in vacuo*. The brown oil was extracted with anhydrous hexane (2 x 75 mL) and filtered through Celite. The hexane was removed *in vacuo* to give an orange oil, which was purified by vacuum distillation. ${}^t\text{BuTe}(\text{CH}_2)_3\text{Te}{}^t\text{Bu}$ was collected as an orange-brown oil at 120°C at 0.1 mmHg. Yield 16.2 g, (78%). ${}^1\text{H}$ NMR (CDCl_3 , 295 K) δ /ppm: 1.48 (s, [18H], CH_3), 2.11 (m, [2H], TeCH_2), 2.63 (t, [4H], TeCH_2CH_2). ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (CDCl_3 , 295 K) δ /ppm: 35.73 (CTe), 34.28 (TeCH_2), 23.08 (TeCH_2CH_2), 5.75 (CH_3). ${}^{125}\text{Te}\{{}^1\text{H}\}$ NMR (CDCl_3 , 295 K) δ /ppm: 612.

EXAMPLE 3

[GaCl₃(TeⁿBu₂)]

This is an example of an alkyltelluroether precursor for depositing a metal telluride. GaCl₃ (0.29 g, 1.7 mmol) was dissolved in anhydrous CH₂Cl₂ (10 mL) and a solution of TeⁿBu₂ (0.40 g, 1.7 mmol) in anhydrous CH₂Cl₂ (10 mL) was added with stirring. After 30 minutes, all solvent was removed *in vacuo* to give an orange oil, which was washed with cold hexane (5 mL). Yield 0.55 g (80%). ${}^1\text{H}$ NMR (CDCl_3 , 295 K) δ /ppm: 0.99 (t, [6H]), 1.48 (m, [4H]), 1.88 (m, [4H]), 3.08 (t, [4H]). ${}^{71}\text{Ga}$ NMR (CDCl_3 , 295 K) δ /ppm: 234 ($W_{1/2}$ = 3500 Hz). IR (cm^{-1} , Nujol): 387 (s,br), 349 (s).

EXAMPLE 4 **$[(\text{GaCl}_3)_2\{\text{}^n\text{BuTe}(\text{CH}_2)_3\text{Te}^n\text{Bu}\}]$**

This is an example of an alkyltelluroether precursor for depositing a metal telluride. GaCl_3 (0.44 g, 2.5 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and a solution of $^n\text{BuTe}(\text{CH}_2)_3\text{Te}^n\text{Bu}$ (prepared according to Example 1) (0.51 g, 2.5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added with stirring to form an orange solution. After 30 minutes, all solvent was removed *in vacuo* to give a viscous brown oil, which was washed with cold hexane (5 mL). Yield 0.67 g (73%). ^1H NMR (CDCl_3 , 295 K) δ /ppm: 1.00 (m, [6H]), 1.50 (m, [4H]), 1.90 (m, [4H]), 2.47 (m, [2H]), 3.09 (m, [4H]), 3.17 (m, [4H]). ^{71}Ga NMR (CDCl_3 , 295 K) δ /ppm: 234 ($W_{1/2}$ = 6000 Hz). IR (cm^{-1} , Nujol): 387 (s,br), 349 (s).

EXAMPLE 5 **$[(\text{GaCl}_3)_2\{\text{}^t\text{BuTe}(\text{CH}_2)_3\text{Te}^t\text{Bu}\}]$**

This is an example of an alkyltelluroether precursor for depositing a metal telluride. GaCl_3 (0.44 g, 2.5 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and a solution of $^t\text{BuTe}(\text{CH}_2)_3\text{Te}^t\text{Bu}$ (prepared according Example 2) (0.51 g, 2.5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added with stirring to form an orange solution. The volume of solvent was reduced *in vacuo* to 10 mL and stored at 5°C overnight. Yellow, needle like crystals grew from the solution. Yield 0.63 g (69%). Anal. Calcd for $\text{C}_{11}\text{H}_{24}\text{Cl}_6\text{Ga}_2\text{Te}_2$: C, 17.3; H, 3.2. Found: C, 17.5, H, 3.0%. ^1H NMR (CDCl_3 , 295 K) δ /ppm: 1.85 (s, [18H]),

CH₃), 2.55 (m, [2H], TeCH₂), 3.14 (t, [4H], TeCH₂CH₂). IR (cm⁻¹, Nujol): 397 (m), 383 (s), 351 (m). Raman (cm⁻¹): 396 (w), 378 (w), 348 (s).

EXAMPLE 6

[SnCl₄{ⁿBuTe(CH₂)₃TeⁿBu}]

This is an example of an alkyltelluroether precursor for depositing a metal telluride. SnCl₄ (0.130 g, 0.5 mmol) was added to solution of ⁿBuTe(CH₂)₃TeⁿBu (prepared according to Example 1) (0.205 g, 0.5 mmol) in anhydrous CH₂Cl₂ (10 mL) either at room temperature or cooled to 0°C (ice bath) with constant stirring. An orange solution was obtained immediately. After stirring for 30 mins., the solution was concentrated *in vacuo* yielding brown precipitate which was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.20 g, 60%. ¹H NMR (CD₃CN) δ/ppm: 1.00 (t, [6H] CH₃), 1.49 (m, [4H], CH₂), 1.70 (br, [4H], CH₂), 3.2–3.6 (br m, [10H], CH₂). IR (Nujol) (ν/cm⁻¹: 292 (sh), 307 (s) Sn–Cl.

EXAMPLE 7

ⁿBuSe(CH₂)₃SeⁿBu

This is an example of a selenoether ligand used to prepare a metal halide complex and to demonstrate the highly selective chemical vapour deposition. Freshly ground selenium powder (5.0 g, 0.063 mol) in dry tetrahydrofuran (140 mL) was frozen in a liquid nitrogen bath. ⁿBuLi (40 mL of 1.6 mol dm⁻³ solution in diethyl ether, 0.063 mol) was added and the mixture

allowed to thaw, and then stirred at room temperature for 2 h to give a colorless solution. 1,3-Dichloropropane (3 mL, 3.57 g, 0.03 mol) was added dropwise to the mixture which was then refluxed 1 h. Hydrolysis (aqueous saturated NaCl, 100 mL) was followed by separation, extraction with diethyl ether and drying (MgSO₄). The solvent was removed by distillation and the residue fractionated *in vacuo* to give pale yellow oil. Yield: 5.0 g, 50%. ¹H NMR (CDCl₃) δ/ppm: 0.90 (t, [6H], CH₃), 1.39 (m, [4H], CH₂), 1.62 (m, [4H], CH₂), 1.97 (m, [2H], CH₂), 2.54 (m, [4H], CH₂Se), 2.62 (s, [4H], SeCH₂). ¹³C{¹H} NMR (CDCl₃) δ/ppm: 13.59 (CH₃), 23.02 (CH₂), 23.56 (CH₂Se, ¹J_{SeC} = 60 Hz), 23.75 (CH₂Se, ¹J_{SeC} = 60 Hz), 31.26 (CH₂), 32.71 (CH₂). ⁷⁷Se{¹H} NMR (neat) δ/ppm: 156.

EXAMPLE 8

ⁿBuSe(CH₂)₂SeⁿBu

This is an example of a selenoether ligand used to prepare a metal halide complex and to demonstrate the highly selective chemical vapour deposition. Prepared as in Example 8, but using 1,2-dichloroethane. Yield: 5.0 g, 50%. ¹H NMR (CDCl₃) δ/ppm: 0.92 (t, [6H], CH₃), 1.42 (m, [4H], CH₂), 1.66 (m, [4H], CH₂), 2.62 (m, [4H], CH₂Se), 2.84(s, [4H], SeCH₂). ¹³C{¹H} NMR (CDCl₃) δ/ppm: 13.59 (CH₃), 23.02 (CH₂), 23.80 (CH₂Se, ¹J_{SeC} = 60 Hz), 23.93 (CH₂Se, ¹J_{SeC} = 61 Hz), 32.78 (CH₂). ⁷⁷Se{¹H} NMR (neat) δ/ppm: 205.

EXAMPLE 9

[SnCl₄{ⁿBuSe(CH₂)₂SeⁿBu}]

This is an example of a metal halide complex used to demonstrate the highly selective chemical vapour deposition. SnCl₄ (0.260 g, 1.00 mmol) was added to solution of ⁿBuSe(CH₂)₂SeⁿBu (0.300 g, 1.00 mmol) in anhydrous CH₂Cl₂ (10 mL) at room temperature with constant stirring. A pale yellow solution was obtained immediately. After stirring for 30 mins., the solution was concentrated *in vacuo* yielding an off-white precipitate which collected by filtration, was washed with hexane and dried *in vacuo*. Crystals were obtained by cooling the CH₂Cl₂ filtrate from the reaction synthesis at *ca.* -18°C. Yield: 0.35 g, 62%. Anal. Calcd for C₁₀H₁₂Cl₄Se₂Sn·0.5CH₂Cl₂: C 20.9, H 3.6. Found: C 20.7, H 3.8%. ¹H NMR (CDCl₃, 298 K) δ/ppm: 0.91 (t, [6H], CH₃), 1.42 (m, [4H], CH₂), 1.78 (m, [4H], CH₂), 3.03 (s, [4H], SeCH₂), 3.28 (m, [4H], SeCH₂CH₂Se), 5.30 (CH₂Cl₂); (193 K) δ/ppm: 0.91 (t, [6H], CH₃), 1.42 (m, [4H], CH₂), 1.76 (m, [4H], CH₂), 3.15 (m, [4H], SeCH₂), 3.60 (m, [4H], SeCH₂CH₂Se), 5.34 (CH₂Cl₂). ¹¹⁹Sn NMR (CH₂Cl₂/CDCl₃, 298 K): no resonance observed; (193 K) δ/ppm: -626, -649 (ratio ~3:1). ⁷⁷Se{¹H} NMR (CH₂Cl₂, 298 K): no resonance observed; (193 K) δ/ppm: 201, 231 (ratio ~3:1). IR (Nujol) ν/cm⁻¹: 264 (w), 309 (s), 320 (s) Sn-Cl. Raman ν/cm⁻¹: 236 (s), 264 (s), 319 (s) Sn-Cl. Crystals of this compound suitable for single-crystal X-ray analysis were obtained by cooling the filtrate (CH₂Cl₂) from the complex preparation. Data collection used a Bruker-Nonius Kappa CCD diffractometer fitted with monochromated Mo-Kα radiation (λ=0.71073 Å), with the crystals held at 120 K in a nitrogen gas stream. Structure solution and

refinement were straightforward, with H atoms introduced into the model in idealized positions. Crystal structure of $[\text{SnCl}_4\{\text{}^n\text{BuSe}(\text{CH}_2)_2\text{Se}^n\text{Bu}\}]$, (1): formula = $\text{C}_{10}\text{H}_{22}\text{Cl}_4\text{Se}_2\text{Sn}$, $M = 560.69$, crystal system monoclinic, space group $\text{C}2/c$ (no. 15), $a = 9.186(2)$, $b = 11.811(4)$, $c = 17.1785(10)$ Å, $\beta = 102.432(4)^\circ$, $1820.0(7)$ Å³, $\mu = 5.972$ mm⁻¹, total no. of reflections measured = 7590, $R_{\text{int}} = 0.0455$, 2079 unique reflections, 79 independent parameters, $R1$ ($I > 2\sigma I$) = 0.0336, $R1$ (all data) = 0.040, $wR2$ ($I > 2\sigma I$) = 0.075, $wR2$ (all data) = 0.079.

EXAMPLE 10

$[\text{SnCl}_4\{\text{}^n\text{BuSe}(\text{CH}_2)_3\text{Se}^n\text{Bu}\}]$

This is an example of a metal halide complex used to demonstrate the highly selective chemical vapour deposition. SnCl_4 (0.130 g, 0.5 mmol) was added to solution of ${}^n\text{BuSe}(\text{CH}_2)_2\text{Se}^n\text{Bu}$ (0.157 g, 0.5 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature with constant stirring. A yellow solution was obtained immediately. After stirring for 30 mins., the solution was concentrated *in vacuo* yielding pale yellow precipitate which was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.19 g, 65%. Calc. For $\text{C}_{11}\text{H}_{24}\text{Cl}_4\text{Se}_2\text{Sn}$: C 22.9, H 4.2. Found: C 23.6, H 4.5%. ${}^1\text{H}$ NMR (CDCl_3 , 298 K) δ/ppm : 0.98 (t, [6H], CH_3), 1.48 (m, [4H], CH_2), 1.83 (m, [4H], CH_2), 2.53 (m, [2H], CH_2), 3.30 (m, [4H], CH_2Se), 3.41 (m, [4H], SeCH_2). ${}^{119}\text{Sn}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$, 298 K): no resonance observed; (190 K) δ/ppm : -695 (${}^1J_{\text{SnSe}} = 505$ Hz). ${}^{77}\text{Se}\{{}^1\text{H}\}$ NMR (CD_2Cl_2 , 185 K) δ/ppm : 290. IR (Nujol) ν/cm^{-1} : 311

(br) Sn–Cl. Raman ν/cm^{-1} : 270 (s), 319 (s) Sn–Cl. Thermogravimetric analysis (performed in a dry, N_2 purged glove box) shows complete sublimation, with $T_{\text{sub}} = 563 \text{ K}$.

EXAMPLE 11

[BiCl₃(TeⁿBu₂)₃]

This is a alkyltelluroether complex used to demonstrate the highly selective chemical vapour deposition of a metal telluride. BiCl₃ (0.15 g, 0.48 mmol) was dissolved in CH₃CN (10 mL) and the solution cooled to 0 °C. A solution of TeⁿBu₂ (0.35 g, 1.44 mmol) in CH₃CN (10 mL) was slowly added to the cooled BiCl₃ solution causing an immediate orange colour which darkened to red. The solution was stirred at 0 °C for 30 min then the volatile components were removed under vacuum, resulting in a viscous red oil which was dried under vacuum for 1 h. Yield = 0.39 g, 79 %. Required for C₂₄H₅₄BiCl₃Te₃: C, 27.7; H, 5.2. Found: C, 27.6; H, 5.3 %. ¹H NMR (CDCl₃): 0.96 (t, [3H], CH₃), 1.46 (m, [2H], CH₂), 1.81 (q, [2H], CH₂), 3.24 (t, [2H], CH₂Te). ¹³C{¹H} NMR (CDCl₃): 11.9, 13.5, 25.1, 33.6. ¹²⁵Te{¹H} NMR (CDCl₃): 238.5. IR (Nujol /cm⁻¹): 248 (Bi–Cl).

EXAMPLE 12

[GaCl₃(SeⁿBu₂)₃]

This is an example of a metal halide complex used to demonstrate the highly selective chemical vapour deposition. GaCl₃ (0.44 g, 2.5 mmol) was dissolved in anhydrous CH₂Cl₂ (10 mL), and a solution of SeⁿBu₂ (0.48 g, 2.5

mmol) in anhydrous CH_2Cl_2 (5 mL) was added with stirring. After 30 min, all volatiles were removed in vacuo to give a pale yellow oil. Yield = 0.75 g, 82%. Anal. Calcd for $\text{C}_8\text{H}_{18}\text{Cl}_3\text{GaSe}$: C, 26.0; H, 4.9. Found: C, 26.7, H, 5.7%. ^1H NMR (CDCl_3 , 295 K): 0.98 (t, [6H], CH_3), 1.50 (m, [4H], CH_2), 1.86 (m, [4H], CH_2), 3.16 (t, [4H], SeCH_2). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 295 K): 135. ^{71}Ga NMR (CD_2Cl_2 , 295 K): 244 ($W_{1/2} \sim 9000$ Hz). IR (cm^{-1} , neat film): 395 (s), 371 (s), 356 (s). Raman (cm^{-1}): 396 (w), 373 (w), 355 (s).

EXAMPLE 13

[GaBr₃(SeⁿBu₂)]

This is an example of a metal halide complex used to demonstrate the highly selective chemical vapour deposition. This was prepared similarly from Se^nBu_2 and GaBr_3 (0.100 g, 0.32 mmol) in anhydrous CH_2Cl_2 . Orange oil. Yield = 0.152 g, 94%. Anal. Calcd for $\text{C}_8\text{H}_{18}\text{Br}_3\text{GaSe}$: C, 19.1; H, 3.6. Found: C, 19.6; H, 3.7%. ^1H NMR (CDCl_3 , 295 K): 0.99 (t, [6H], CH_3), 1.49 (m, [4H], CH_2), 1.87 (m, [4H], CH_2), 3.08 (t, [4H], SeCH_2). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CDCl_3 , 295 K): 146. ^{71}Ga NMR (CDCl_3 , 295 K): 125 ($W_{1/2} \sim 4200$ Hz). IR (cm^{-1} , neat film): 299 (s), 237 (m). Raman (cm^{-1}): 285 (m), 235 (s).

EXAMPLE 14

Metal Telluride Film Characterization

This Example describes the instruments used for collection of X-Ray diffraction patterns of the metal telluride films produced from the

alkyltelluroether precursors. Data were collected in grazing incidence ($\theta_i=3^\circ$) using a Bruker D8 with GADDS diffractometer or using a Rigaku SmartLab diffractometer (Cu $K_{\alpha 1}$). Scanning electron microscopy was performed on samples of the metal telluride films at an accelerating voltage of 10 kV using a Zeiss EVO LS 25, and energy dispersive X-ray data were obtained on the metal telluride films with an Oxford INCAx-act X-ray detector attached.

EXAMPLE 15

Substrate preparation and pre-treatment

This Example describes the preparation and pre-treatment of the substrates onto which the metal tellurides were deposited. TiN films with thickness of 100 nm were deposited on a p-type Si (100) wafer by the medium frequency magnetron sputtering method at room temperature (type: Leybold HELIOS Pro). The films were deposited under a Ti (99.99% purity) target with a DC power of 3000 W in a N_2/Ar atmosphere. The N_2 and Ar flow rates were maintained at 30 and 35 sccm respectively. A high drive speed of 180 rpm was applied to enhance the film uniformity. The deposition rate was found to be 0.161 nm s^{-1} . SiO_2 films with thickness of $1 \mu\text{m}$ were also formed by the medium frequency magnetron sputtering method using a pure Si (99.99% purity) target with a DC power of 2000 W in an O_2/Ar atmosphere. The O_2 and Ar flow rates were maintained at 20 sccm and 40 sccm respectively. With the same drive speed of 180 rpm, the deposition rate was 0.3 nm s^{-1} . The patterned samples were fabricated via a photolithographic process followed by a reactive-ion etching of SiO_2 . The pattern was pre-

designed on a mask with template hole-sizes ranging from 1 μm to 100 μm . The photolithography was carried out using an EVG 620TB with a positive resist S1813. The etching was performed by a RIE80+ with CHF_3 and Ar. The etching rate was found to be 22 nm s^{-1} .

The silica tile substrates (ca. $1 \times 5 \times 25 \text{ mm}$) used for the depositions were previously cleaned with acetone and demineralised water and dried at 100°C overnight. Prior to low pressure chemical vapour deposition experiments the silicon tiles ($1 \times 5 \times 25\text{mm}$) were suspended over 40% HF solution for 15 mins., then immediately transferred to a Schlenk tube and heated *in vacuo* at 110°C for ca. 6 hours to ensure complete removal of surface bound H_2O (this completely eliminated tin oxide formation during subsequent deposition experiments). Patterned TiN/SiO_2 substrates were similarly etched with HF vapour, but for three mins. only.

EXAMPLE 16

Low Pressure Chemical Vapour Deposition onto un-patterned substrates using alkyltelluroether precursor products according to Examples 3, 4 and 11.

The alkyltelluroether precursor (5 – 100 mg) and substrates were loaded into a closed-end silica tube in a glove-box (precursor at the closed end, followed by either Si, SiO_2 or TiN substrates positioned end-to-end through the heated region). The tube was set in a furnace such that precursor was outside the heated zone, the tube was evacuated, then heated to 773 K (actual temperature in the hot zone ca. 767 K) under 0.05 mmHg and the

furnace was allowed to stabilize. The tube position was then adjusted so that the precursor was moved towards the hot zone (T ca. 465 K based on temperature profiling carried out after deposition). At this point the sample position was maintained until the solid precursor had melted and completely evaporated (no residual precursor remained), ca. 30 mins. The tube was then cooled to room temperature and transferred to the glove box where the tiles were removed and stored under an N_2 atmosphere prior to analysis. The highest degree of substrate coverage was found just outside the furnace hot zone and ~100 mm from the precursor, where the temperature was ca. 753 – 773 K, and these were the films selected for further study. Similar experiments were conducted at 50 degree intervals between 723 and 823 K and using variable amounts of precursor to control the film thickness.

The alkyltelluroether precursors produced according to Examples 3 and 4 gave Ga_2Te_3 , the alkyltelluroether precursor produced according to Example 11 gave Bi_2Te_3 , the alkylselenoether precursors according to Examples 9 and 10 gave $SnSe_2$ films, while the alkylselenoether precursors according to Examples 12 and 13 gave Ga_2Se_3 films, with no significant differences in appearance or properties observed across the deposition temperatures used. Deposited films were generally very well adhered to the substrates. Excellent reproducibility was obtained and metal telluride and metal selenide films were visually very similar between depositions conducted across the temperature range. Similar characterization data were obtained from several different samples of the metal telluride and metal selenide films.

EXAMPLE 17

Low Pressure Chemical Vapour Deposition onto patterned TiN/SiO₂ or Si/SiO₂ substrates using alkylselenoether precursor produced according to Examples 9 and 10

TiN/SiO₂ and Si/SiO₂ patterned substrates (1 x 5 x 25 mm), the latter previously pre-treated by HF vapor-etching for 3 mins. and dried *in vacuo* at 110°C for ca. 6 hours, were loaded with 5 mg of alkylselenoether precursor into a closed-end silica tube in a glove-box as described above, and depositions were performed similarly. A similar process was able to be used for the alkyltelluroether precursor described in Examples 3, 4 and 11.

EXAMPLE 18

Hall measurements on metal telluride films obtained using the procedure described in Example 15 and using the alkyltelluroether precursor described in Example 3.

Hall measurements were performed at room temperature on a Nanometrics HL5500PC with a current of 1 mA. For these measurements, the metal chalcogenides film was deposited on a SiO₂/Si substrate to insulate the current to the substrate. Experiments were conducted under a magnetic field of 0.5 T at 300 K. Hall measurements for Ga₂Te₃ obtained from Example 3: p-type semiconductor; resistivity 195±10 Ωcm; carrier density of 5 × 10¹⁵ cm⁻³.

A similar process was able to be used for the Bi₂Te₃ film obtained using the alkyltelluroether precursor described in Example 11. The resistivities for the

Bi₂Te₃ films: 5.65×10^{-4} (± 0.016) Ω cm; n-type semiconductor; carrier density of 1.95×10^{20} cm⁻³; Seebeck coefficient: -108 (film thickness = 0.872 μ m). A similar process was able to be used for the SnSe₂ film obtained using the alkylselenoether precursors described in Examples 9 and 10. The resistivities for the SnSe₂ films were found to be 210 (± 10) m Ω cm; n-type semiconductor; carrier density of 5.0×10^{18} cm⁻³.

The moisture-sensitive alkyltelluroether precursors [GaCl₃(TeⁿBu₂)] [(GaCl₃)₂{ⁿBuTe(CH₂)₃TeⁿBu}] and [(GaCl₃)₂{^tBuTe(CH₂)₃Te^tBu}], prepared according to Examples 3, 4 and 5 were obtained in good yield by direct reaction of GaCl₃ with the ligand in anhydrous CH₂Cl₂. The solids were stored in a freezer and manipulated in an N₂ purged, dry (< 1 ppm H₂O) glove-box and were characterized by IR, Raman, variable temperature ¹H, ⁷¹Ga and ¹²⁵Te{¹H} NMR spectroscopy and microanalysis as appropriate. The spectroscopic features of the new complexes were in accord with those of related complexes in the literature. The crystal structure of the precursor produced according to Example 5 showed a dinuclear molecule with three Cl ligands on each gallium and a bridging ditelluroether.

The alkyltelluroether precursor [BiCl₃{TeⁿBu₂}₃] prepared according to Example 11 was obtained similarly from BiCl₃ and TeⁿBu₂ in anhydrous CH₂Cl₂ and characterised by IR, ¹H and ¹²⁵Te{¹H} NMR spectroscopy.

The moisture-sensitive alkylselenoether precursors [SnCl₄{ⁿBuSe(CH₂)_nSeⁿBu}], prepared according to Examples 9 and 10, were obtained in good yield by direct reaction of SnCl₄ with the ligand in anhydrous CH₂Cl₂. The solids were stored and manipulated in an N₂ purged, dry (< 1

ppm H₂O) glove-box and were characterized by IR, Raman, variable temperature ¹H, ⁷⁷Se{¹H} and ¹¹⁹Sn NMR spectroscopy and microanalysis as appropriate. The spectroscopic features of the new complexes were in accord with those of related complexes in the literature. The crystal structure of the precursor produced according to Example 9 showed a discrete mononuclear molecule with four mutually *cis* Cl ligands and a chelating diselenoether. The complex had crystallographic two-fold symmetry (the Sn atom lies on the C₂ axis) which placed the ⁿBu groups in the *DL* configuration (i.e. the substituents were on opposite sides of the SnSe₂ plane), and the bond distances and angles around the tin atom were in accord with similar Sn(IV) selenoether species.

In order to further illustrate the present invention, reference will now be made to the following Figures in which:

Figure 1 shows the crystal structure of [(GaCl₃)₂{^tBuTe(CH₂)₃Te^tBu}]. Carbon atoms are unlabelled and hydrogen atoms have been omitted for clarity;

Figure 2 shows the X-ray diffraction pattern from Ga₂Te₃ deposited by low pressure chemical vapour deposition on TiN from 100 mg [GaCl₃(TeⁿBu₂)] (Example 3) at 773 K;

Figure 3 shows a scanning electron micrograph image of deposited thin film of Ga₂Te₃ deposited by low pressure chemical vapour deposition on TiN from 100 mg [GaCl₃(TeⁿBu₂)] (Example 3) at 773 K;

Figure 4 shows the X-ray diffraction pattern obtained from Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 723 K;

Figure 5 shows a scanning electron micrograph image of the Ga_2Te_3 film deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 723 K;

Figure 6 shows the X-ray diffraction pattern from Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 823 K;

Figure 7 shows a scanning electron micrographs from Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 823 K;

Figure 8 shows the X-ray diffraction pattern from Ga_2Te_3 deposited on SiO_2 from 50 mg $[(\text{GaCl}_3)_2\{\text{Te}^n\text{BuTe}(\text{CH}_2)_3\text{Te}^n\text{Bu}\}]$ (Example 4) at 773 K;

Figure 9 shows scanning electron micrograph images of Bi_2Te_3 deposited on SiO_2 from 100 mg $[\text{BiCl}_3(\text{Te}^n\text{Bu}_2)_3]$ (Example 11) and 723 K;

Figure 10 shows the X-ray diffraction pattern from Bi_2Te_3 deposited on SiO_2 from 100 mg $[\text{BiCl}_3(\text{Te}^n\text{Bu}_2)_3]$ (Example 11) and 723 K;

Figure 11 shows the Raman spectrum of Bi_2Te_3 deposited on SiO_2 from 100 mg $[\text{BiCl}_3(\text{Te}^n\text{Bu}_2)_3]$ (Example 11) and 723 K;

Figure 12 shows the crystal structure of the precursor produced according to Example 9 and with the atom numbering scheme;

Figure 13 shows scanning electron micrograph images of hexagonal SnSe_2 ;

Figure 14 shows the X-ray diffraction patterns of a thick film and a thin film of SnSe_2 ;

Figure 15 shows the Raman spectrum of SnSe₂ thin film;

Figure 16 shows X-ray photoelectron spectra obtained from a representative deposited film of SnSe₂ on a SiO₂ substrate (a) Sn 3d and (b) Se 3d;

Figure 17 shows a scanning electron micrograph image showing selective growth of SnSe₂ onto the SiO₂ on a patterned Si (left) / SiO₂ (right) substrate;

Figure 18 shows photolithographically patterned SiO₂ / TiN substrates;

Figure 19 shows scanning electron micrograph images and energy dispersive X-ray element maps of SnSe₂ deposited selectively onto TiN within 80 μm diameter holes on TiN/SiO₂;

Figure 20 shows scanning electron micrograph images and energy dispersive X-ray element maps of SnSe₂ deposited selectively onto TiN within 5 μm diameter holes on TiN/SiO₂;

Figure 21 shows a scanning electron micrograph image of SnSe₂ deposited selectively onto TiN within 5 μm diameter holes on TiN/SiO₂;

Figure 22 shows scanning electron micrograph images Ga₂Te₃ deposited preferentially onto TiN within holes on TiN/SiO₂;

Figure 23 shows scanning electron micrograph images and energy dispersive X-ray element maps of Bi₂Te₃ deposited selectively onto TiN within 80 μm diameter holes on TiN/SiO₂;

Figure 24 shows a scanning electron micrograph image images and energy dispersive X-ray element maps of Bi_2Te_3 deposited selectively onto TiN within 2 μm diameter holes on TiN/ SiO_2 ; and

Figure 25 shows a scanning electron micrograph image of Bi_2Te_3 deposited selectively onto TiN within 2 μm diameter holes on TiN/ SiO_2 .

Referring now to the drawings, Figure 1 is a view of the crystal structure of the precursor in Example 4.

Low pressure chemical vapour deposition of the alkyltelluroether precursor in Example 3 and Example 4 was undertaken with the furnace temperature set at 723 and 823 K, leading to clean evaporation of the precursor compound and deposition of yellow film onto the SiO_2 substrate. Similar behaviour was also observed on TiN tiles.

Figure 2 shows the X-ray diffraction pattern from a reflective grey film of Ga_2Te_3 deposited by low pressure chemical vapour deposition on TiN from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 773 K, 0.1 mmHg onto SiO_2 . This confirms a cubic lattice with space group F-43m. Figure 3 shows a scanning electron micrograph image of the same thin film of Ga_2Te_3 deposited by low pressure chemical vapour deposition on TiN from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 773 K.

Figure 4 shows the X-ray diffraction pattern obtained from Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 723 K, 0.1 mmHg onto SiO_2 . This confirms a cubic lattice with space group F-43m.

Figure 5 shows a scanning electron micrograph image of the same Ga_2Te_3 film deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 723 K, 0.1 mmHg.

Figure 6 shows the X-ray diffraction pattern from Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 823 K, 0.1 mmHg onto SiO_2 . This confirms a cubic lattice with space group F-43m. Figure 7 shows a scanning electron micrograph from the same Ga_2Te_3 deposited on SiO_2 from 100 mg $[\text{GaCl}_3(\text{Te}^n\text{Bu}_2)]$ (Example 3) at 823 K.

Figure 8 shows the X-ray diffraction pattern from a silvery grey Ga_2Te_3 film deposited on SiO_2 from 50 mg $[(\text{GaCl}_3)_2\{\text{}^n\text{BuTe}(\text{CH}_2)_3\text{Te}^n\text{Bu}\}]$ (Example 4) at 773 K, 0.1 mmHg.

Low pressure chemical vapour deposition of the alkylselenoether complexes in Examples 9 and 10 was undertaken with the furnace temperature set at a range of temperatures (50 degree intervals) between 673 and 823 K, leading to clean evaporation of the precursor compound and deposition of reflective, silvery-black films onto the SiO_2 substrate. Similar behaviour was also observed on TiN tiles.

Figure 9 shows scanning electron micrographs of the films of Bi_2Te_3 obtained by low pressure chemical vapour deposition from the alkyltelluroether precursor described in Example 11, revealing the rhombohedral single crystals coating the SiO_2 surface of the substrate, as well as an isolated single crystal.

Figure 10 shows the X-ray diffraction pattern obtained from the Bi_2Te_3 thin film grown as described, while the Raman spectrum is shown in Figure 11.

Figure 12 is a view of the crystal structure of the precursor in Example 10 with atom numbering scheme. H atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level ellipsoids. The molecule has 2-fold symmetry. Symmetry operation: $a = 1 - x, y, 1/2 - z$.

Low pressure chemical vapour deposition of both alkylselenoether complexes in Examples 9 and 10 was undertaken with the furnace temperature set at a range of temperatures (50 degree intervals) between 673 and 823 K, leading to clean evaporation of the precursor compound and deposition of reflective, silvery-black films onto the SiO_2 substrate. Similar behaviour was also observed on TiN tiles and clean, dried (after etching with HF vapour) Si tiles. Initially depositions used *ca.* 50 to 100 mg of precursor, producing films of thickness *ca.* 40 to 60 μm for compositional and structural characterization. Later depositions were reagent-limited (2 – 5 mg) to produce films with thicknesses in the range 0.5 to 2 μm . Scanning electron microscopy analysis on the SnSe_2 films showed a regular morphology formed of hexagonal plate crystallites (Figure 13a and b) and cross-sectional SEM images of typical films grown at between 673 and 823 K using 100 mg of precursor showed these were ~40 to 60 μm thick. In these films the growth direction of the crystallites is quite random, but with a significant percentage aligned approximately perpendicular to the substrate surface. In contrast,

reagent-limited films grown using 0.005 g of precursor (30 mins.) were much thinner as expected (1 to 2 μm), and scanning electron microscopy image Figure 13c shows the majority of crystallites lying flat on the substrate surface, consistent with the preferred orientation seen by XRD analysis (below); the individual crystallites are *ca.* 1.6 μm x 2.0 μm across the hexagon as shown in Figure 13d. Atomic force microscopy measurements were consistent with the scanning electron microscopy data, revealing that the thicker SnSe_2 film surfaces are considerably rougher than the 0.5–2 μm samples. Route mean square roughness measurements on the latter are *ca.* 130 nm (2 x 2 micron scan).

Referring to Figure 14, X-ray diffraction measurements on the materials deposited from the precursors produced according to Example 9 and 10 at all temperatures examined confirmed them to be crystalline hexagonal SnSe_2 in all cases, consistent with space group $P-3m1$, $a = 3.82\text{--}3.83$ Å; $c = 6.14\text{--}6.16$ Å (literature values for bulk SnSe_2 : $a = 3.81$ Å; $c = 6.14$ Å) with no evidence for other phases. There is no significant variation in the lattice parameters of this phase with deposition temperature. Strong evidence was seen from the X-ray patterns for preferred orientation of the crystallites in the thick films (in the range 40 to 60 μm), however this is much more pronounced in the thin (1 to 2 μm) films. The X-ray pattern for the thin films is shown in Figure 14, with intense 001 and 002 peaks, suggests that there is a large enhancement along the *c*-axis. For thick films there is also some preferred orientation observed from the diffraction data. In this case the

pattern is closer to the normal powder distribution of intensities as crystallites can be aligned at any angle parallel or perpendicular to a single direction in the plane of the film, but enhancement of the 100 and 110 peaks indicates suppression of the peaks related to c-axis alignment as shown in Figure 14.

Referring to Figure 15, Raman spectra recorded from the thin film sample obtained using Examples 9 and 10 each show one intense (and sharp) band at 182.4 cm^{-1} as shown in Figure 15, which is assigned to the A_{1g} Raman-active mode, and measurements taken at several locations on the sample showed no significant variation in the peak width. These data are also consistent with crystalline hexagonal SnSe_2 .

Figure 16 shows the X-ray photoelectron spectroscopic data obtained from a representative deposited film of SnSe_2 on SiO_2 substrate, (a) Se 3d and (b) Sn 3d using Examples 9 and 10. More specifically, referring to Figure 16, X-ray photoelectron spectroscopic measurements on unetched ~ 40 to $60\text{ }\mu\text{m}$ samples showed only one Sn and Se environment, with binding energies corresponding to those reported for SnSe_2 . For unetched SnSe_2 samples C (39.8 wt%) were also evident, but there is no evidence for SnO_2 , elemental Sn or elemental Se. Argon ion etching for 60 seconds resulted in a significant reduction in the carbon content (to 13.0 wt%). The 1:2 Sn:Se ratio was unaffected by etching.

Selective deposition

For many electronic applications, it is desirable to be able to deposit the chalcogenide alloy selectively onto specific regions of a patterned substrate, e.g. in trenches or holes. Variations in the morphology may also be expected to occur on different substrate types. Hence, deposition experiments were performed under the same conditions onto SiO₂, Si and TiN. While the observed morphology was essentially the same for each substrate type, for SnSe₂ the SEM data suggested denser film growth onto TiN and SiO₂ compared to Si. On this basis a series of reagent-limited low pressure chemical vapour deposition experiments using 2 – 5 mg of precursor (deposition time = 30 mins.) were undertaken onto photolithographically patterned substrates formed of SiO₂/Si. Scanning electron micrograph images of the resulting film (Figure 17) show that SnSe₂ film growth onto the SiO₂ is preferred, resulting in very high selectivity. For device applications selective deposition onto a conducting surface such as TiN is particularly advantageous. Patterned SiO₂/TiN substrates were prepared by growing a layer of SiO₂ (1 µm) onto TiN and photolithographically etched to form an array of holes with a range of diameters from 1 to 100 µm (Figure 18). Low pressure chemical vapour deposition of SnSe₂ using these structured substrates resulted in remarkably high selectivity for film growth onto the exposed (conducting) TiN regions within the holes, but not onto the SiO₂. This was observed both for the large (50 – 100 µm diameter) and also for the smaller (5 µm diameter) holes, as illustrated in Figures 19 and 20 respectively.

Figure 17 shows a scanning electron microscopy image showing selective growth of SnSe_2 onto the SiO_2 on a patterned Si (left) / SiO_2 (right) substrate.

Figure 18 shows an illustration of the photolithographically patterned SiO_2/TiN substrates (the SiO_2 top layer was grown to 1 μm thickness)

Figure 19 shows a scanning electron microscopy image (a) and energy dispersive X-ray element maps (b) – (d) confirming the selective deposition of SnSe_2 occurring only within the holes (80 μm diameter) with growth occurring preferentially onto the TiN surface.

Figure 20 shows a scanning electron microscopy image (a) and energy dispersive X-ray element maps (b) – (d) confirming the selective deposition of SnSe_2 occurring only within the 5 μm diameter hole, i.e. onto the exposed TiN surfaces.

Figure 21 shows a scanning electron microscopy image confirming the selective deposition of crystalline SnSe_2 occurring only within the 5 μm diameter hole, i.e. onto the exposed TiN surfaces.

This unexpected selectivity of the film growth is also observed for 2 μm diameter holes, although at this scale the selectivity is limited by the size of the individual SnSe_2 crystallites ($\sim 1.6 \times 2.0 \mu\text{m}$ across the hexagon), hence while nucleation appears to initiate on the TiN, this then nucleates further crystallite growth onto the SiO_2 .

The reasons for this observed highly selective film growth onto the TiN regions using SiO₂/TiN substrates and onto the SiO₂ surfaces on the Si/SiO₂ patterned tiles most likely arises from differences in the nature of the surfaces. Atomic force microscopy measurements confirm that the surface roughness of the different types of substrate are essentially invariant, however, a strong correlation is observed between the contact angle of a water droplet on the surface and the selectivity of the SnSe₂ deposition on the substrate surfaces. The measured contact angles increase from Si to SiO₂ to TiN (θ° : 29, 58, 74 respectively) and selectivity increasing across this same series. This is consistent with precursor adsorption and crystallite nucleation favoring the more hydrophobic substrates. This remarkable selectivity for film deposition from the single source selenoether ligand complexes onto the highly conducting TiN is very attractive for potential applications of chalcogenide materials in electronic devices.

Figure 22 shows that preferential deposition onto the conductive TiN rather than SiO₂ is also evident for Ga₂Te₃ grown from the precursor described in Example 3, while Figures 23 and 24 shows that very highly selective growth of Bi₂Te₃ into the TiN holes both at 80 μ m and 2 μ m diameter on a patterned TiN/SiO₂ substrate using the precursor described in Example 11, while Figure 25 shows the highly crystalline nature of the Bi₂Te₃ deposited under these conditions.

Importantly, the precursors exhibit a very high degree of selectivity onto lithographically patterned substrates, with deposition strongly preferred

onto the (conducting) TiN on SiO₂/TiN surfaces, and onto the SiO₂ on Si/SiO₂ substrates.

The combination of the highly selective growth onto the conducting TiN surfaces within the lithographically formed holes and the stoichiometric, single phase metal telluride film deposition are highly relevant to the prospective application of these and related single source precursors for metal telluride materials in electronics.

In all aspects of the invention a combination of two or more single source metal halide alkyltelluroether precursors may be used. For example, a combination may be used to produce ternary or higher metal telluride materials. Ternary or higher metal telluride materials may be useful in industry, for example, in the production of phase change memory materials or thermoelectric materials. Further, an alkyltelluroether precursor may be used in combination with an analogous alkylselenoether precursor, to form a selenide-doped metal telluride. Such selenide-doped metal tellurides may be useful in thermoelectric applications.

It is to be appreciated that the Examples and the Figures given above have been given by way of example only and that modifications may be effected. Individual components shown in the Examples and the drawings are not limited to use in their Examples and drawings, and they may be used in other Examples and other drawings and in all aspects of the invention.

CLAIMS

1. An alkyltelluroether precursor for use in the single source chemical vapour deposition of a metal telluride, which alkyltelluroether precursor comprises an alkyltelluroether ligand bonded to a metal halide, which alkyltelluroether precursor comprises at least one alkyl group containing at least two carbon atoms, and which alkyltelluroether precursor has the general formula:



where M = metal

X = a halide

n = 3 or 4, and

y = 1, 2 or 3

alkyl = butyl, propyl, ethyl, trimethylsilyl,
cyclohexyl, cyclopentyl or benzyl.

2. An alkyltelluroether precursor according to claim 1 in which n = 3, and in which M = a p-block element.

3. An alkyltelluroether precursor according to claim 2 in which the p-block element is Ga, In, Al, As, Sb or Bi.

4. An alkyltelluroether precursor according claim 1 in which n = 4, and in which M = a p-block element.

5. An alkyltelluroether precursor according to claim 4 in which the p-block element is Sn or Ge.
6. An alkyltelluroether precursor according to any one of the preceding claims in which X = a chloride or a bromide.
7. An alkyltelluroether precursor according to any one of the preceding claims in which the alkyltelluroether is a mono-telluroether TeR_2 , a di-telluroether $\text{RTe}(\text{CH}_2)_n\text{TeR}$ where $n = 1, 3, 4$ or 5 , or a tri-telluroether $\text{MeE}(\text{CH}_2\text{TeR})_3$ where $E = \text{C}$ or Si , or $\text{RTe}(\text{CH}_2)_3\text{Te}(\text{CH}_2)_3\text{TeR}$, and where R for all of the said alkyltelluroethers = alkyl, cycloalkyl, trimethylsilyl or substituted alkyl.
8. An alkyltelluroether precursor according to any one of the preceding claims in which the butyl is n-butyl, t-butyl, or s-butyl.
9. An alkyltelluroether precursor according to any one of the preceding claims in which the propyl is n-propyl or i-propyl.
10. An alkyltelluroether precursor according to claim 7 in which the alkyltelluroether is a di-telluroether and in which the di-telluroether is $\text{BuTe}(\text{CH}_2)_n\text{TeBu}$, where Bu = n-butyl, t-butyl or s-butyl.

11. An alkyltelluroether precursor according to claim 7 in which the alkyltelluroether is a di-telluroether, and in which the di-telluroether is $\text{PrTe}(\text{CH}_2)_n\text{TePr}$, where Pr = i-propyl or n-propyl.
12. A process of producing a metal telluride using at least one alkyltelluroether precursor according to Claim 1, which process comprises placing the precursor together with a substrate into a chemical vapour deposition apparatus, and heating to a predetermined temperature and pressure until the precursor has evaporated and the metal telluride has been deposited on the substrate.
13. A process according to Claim 12 in which the pre-determined temperature and pressure of 600-900 K, 0.1 mmHg, until the precursor had completely evaporated.
14. A process according to Claim 12 or Claim 13 in which the substrate is lithographically patterned TiN/SiO₂ or Si/SiO₂.
15. A process according to any one of claims 12-14 in which there is only one of the alkyltelluroether precursors.
16. A process according to any one of claims 12-14 in which there are two of the alkyltelluroether precursors.

17. A process according to any one of claims 12-14 in which the metal telluride is a selenide-doped metal telluride, and in which the process comprises using the alkyl telluroether precursor according to Claim 1, together with the analogous alkyl selenoether precursor.

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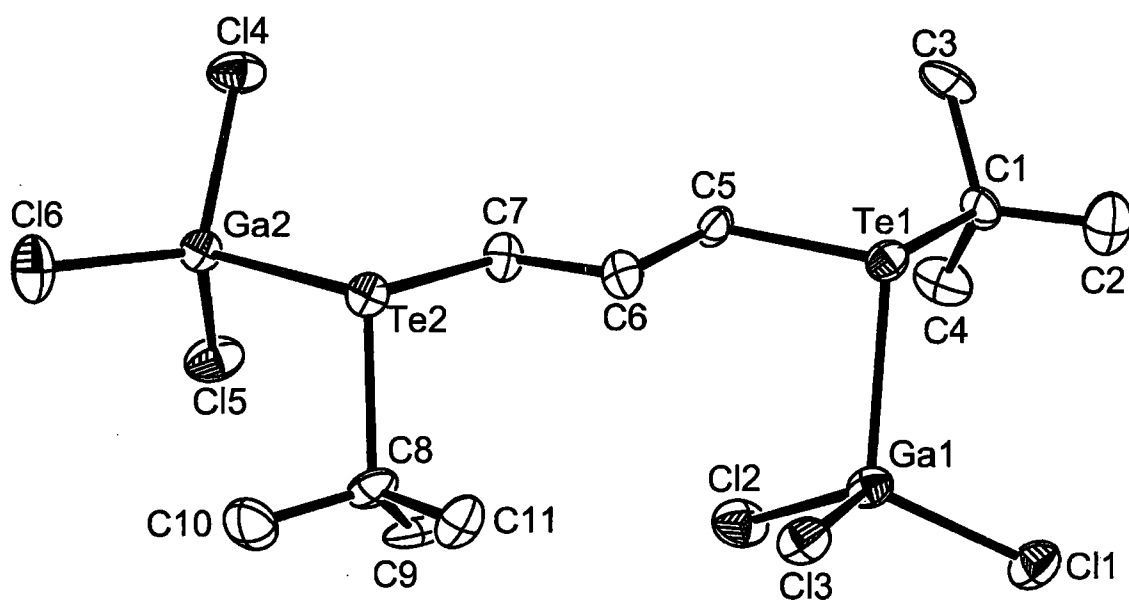


Figure 1

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Counts
(arbitrary)

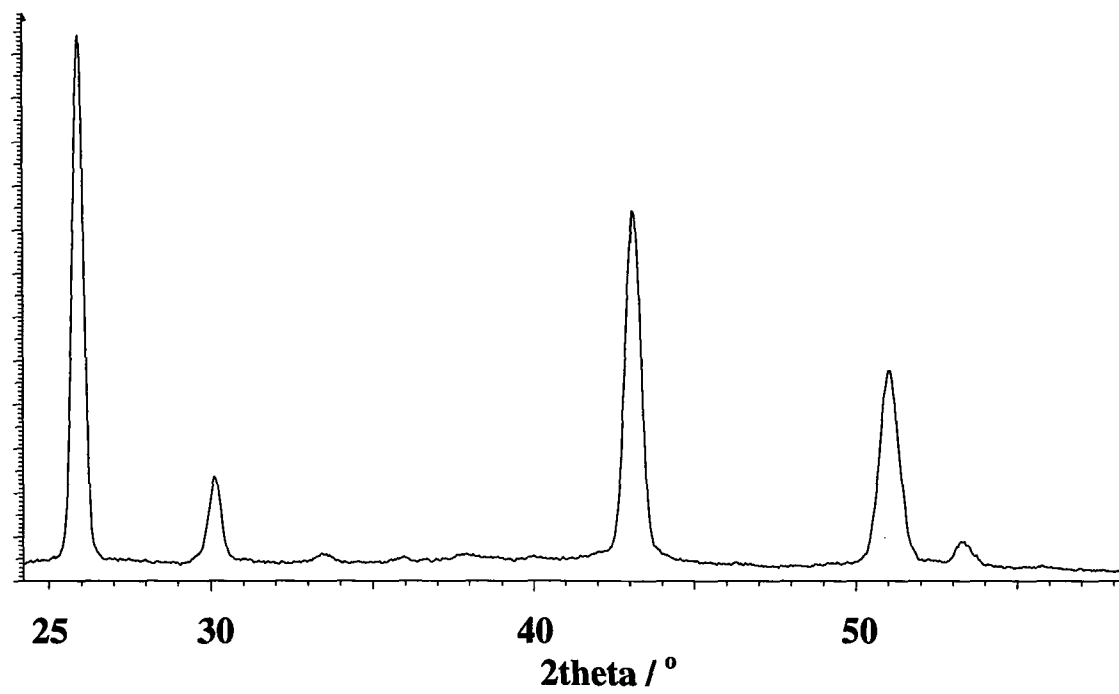


Figure 2

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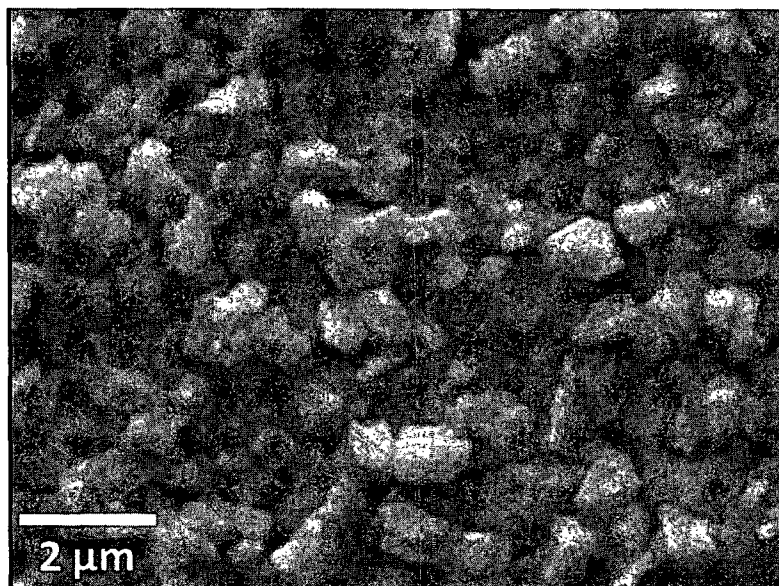


Figure 3

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Counts
(arbitrary)

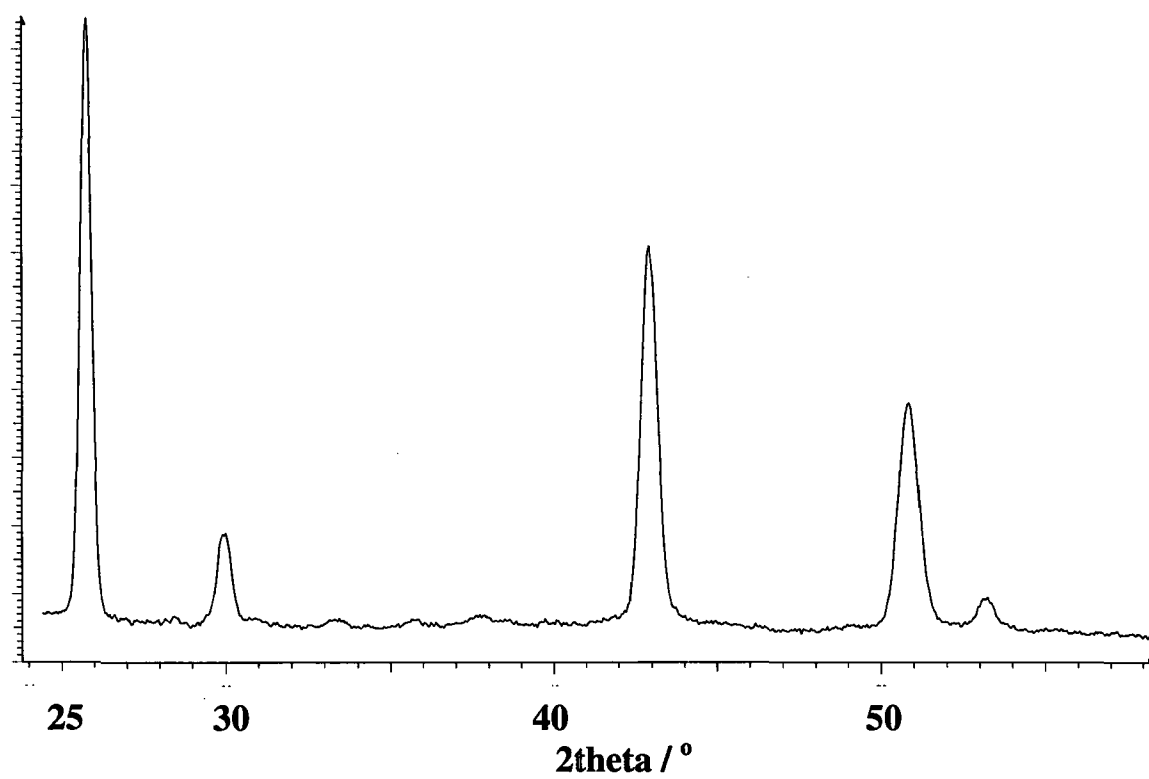


Figure 4

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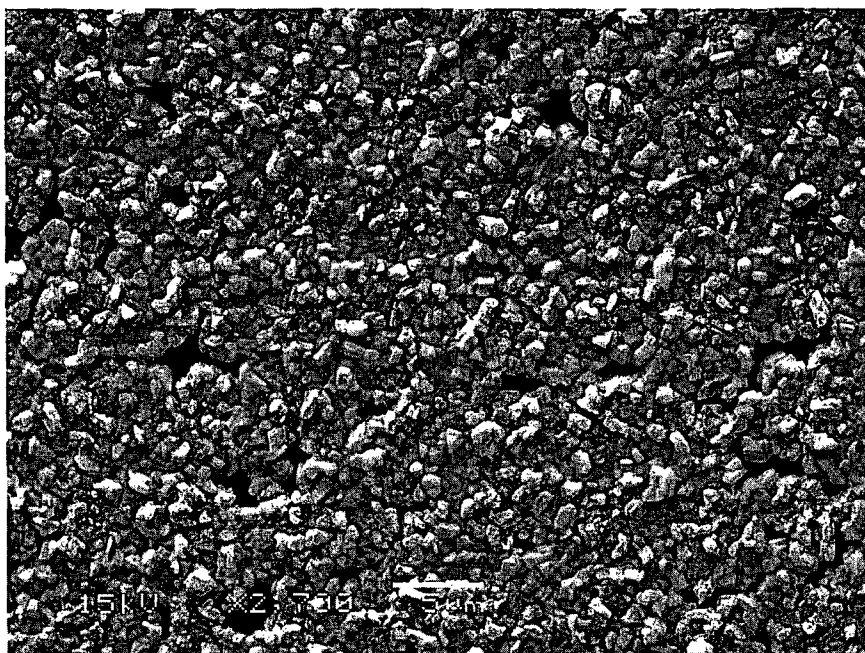


Figure 5

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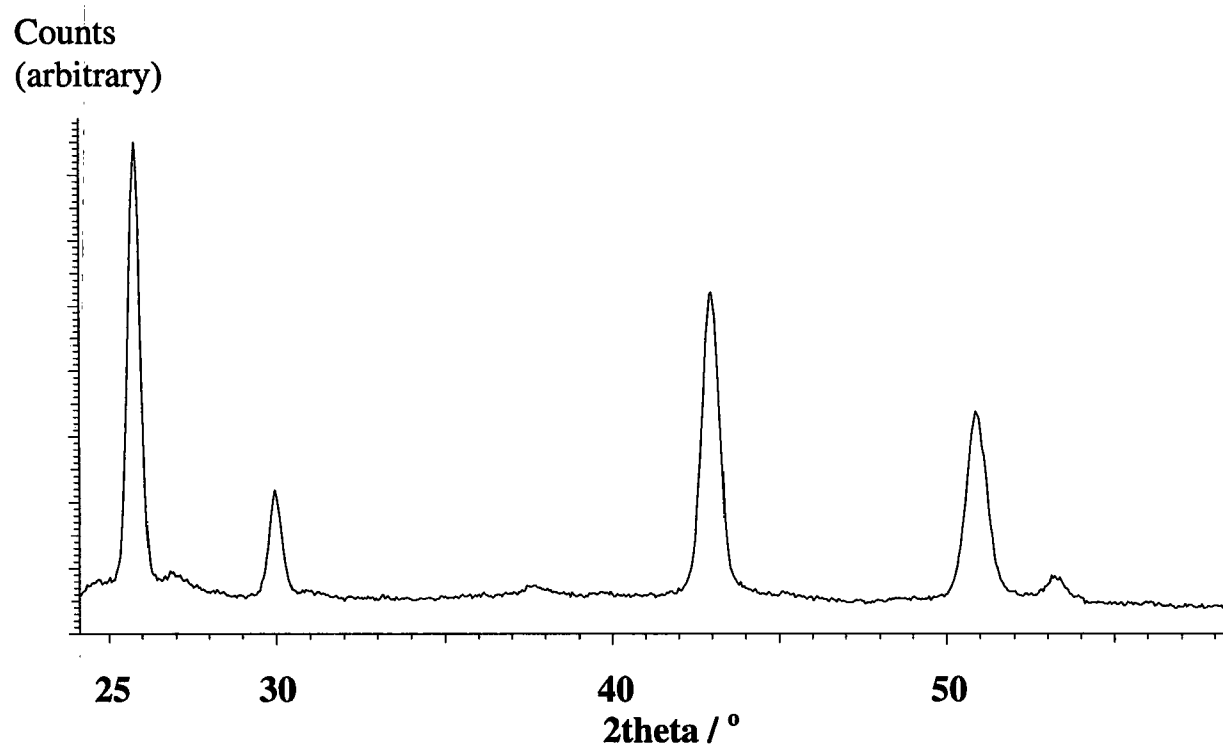


Figure 6

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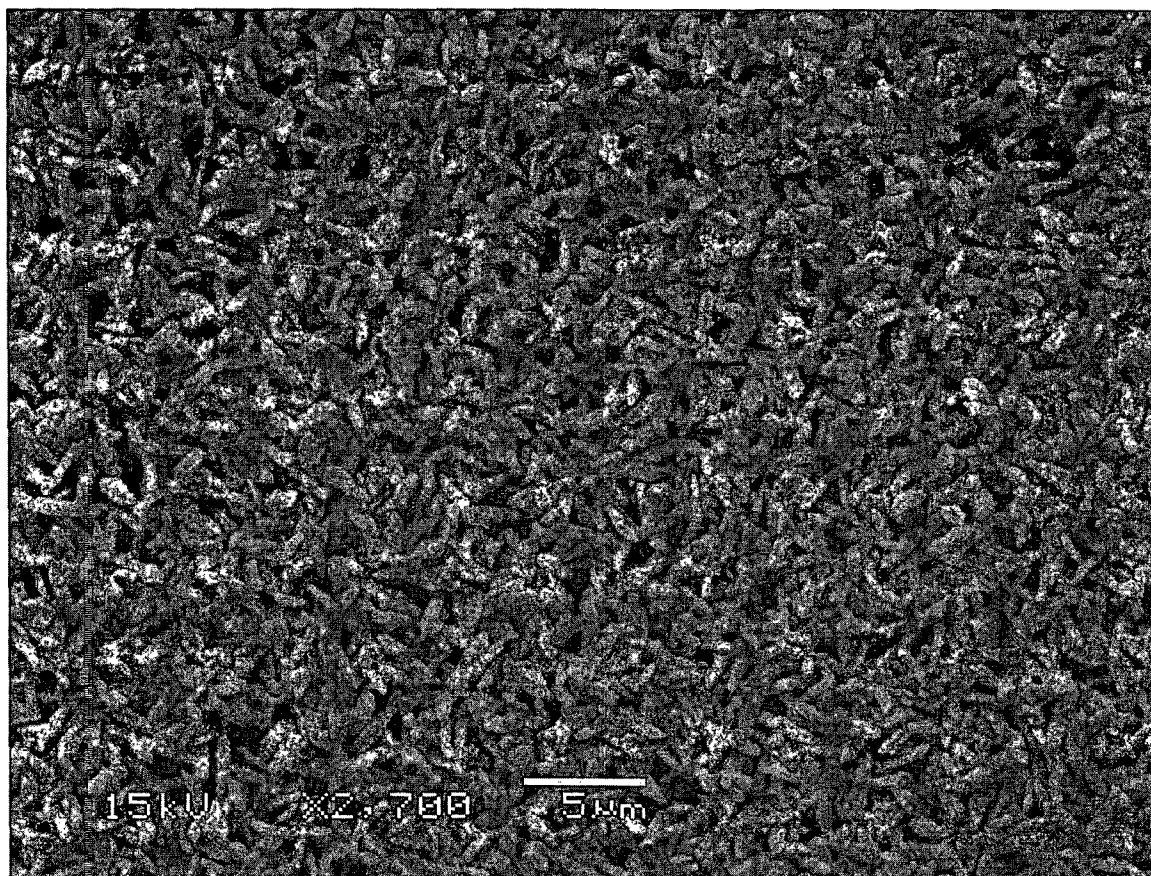


Figure 7

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Counts
(arbitrary)

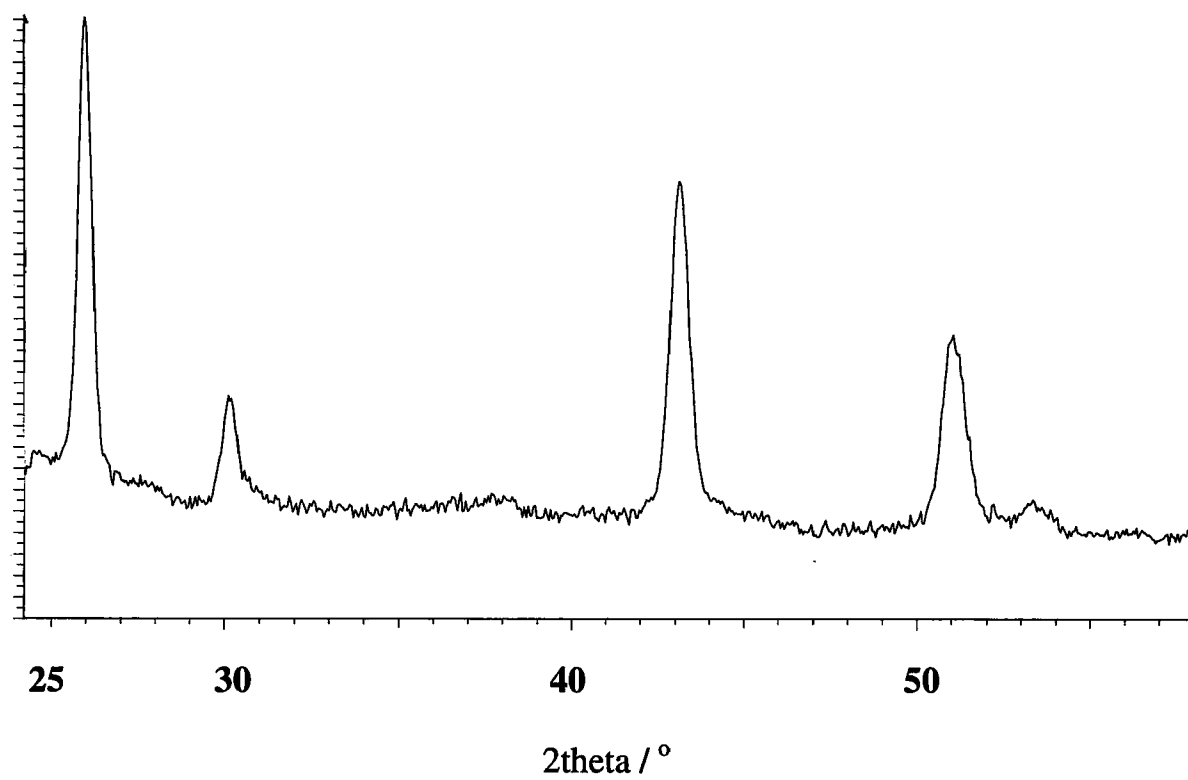


Figure 8

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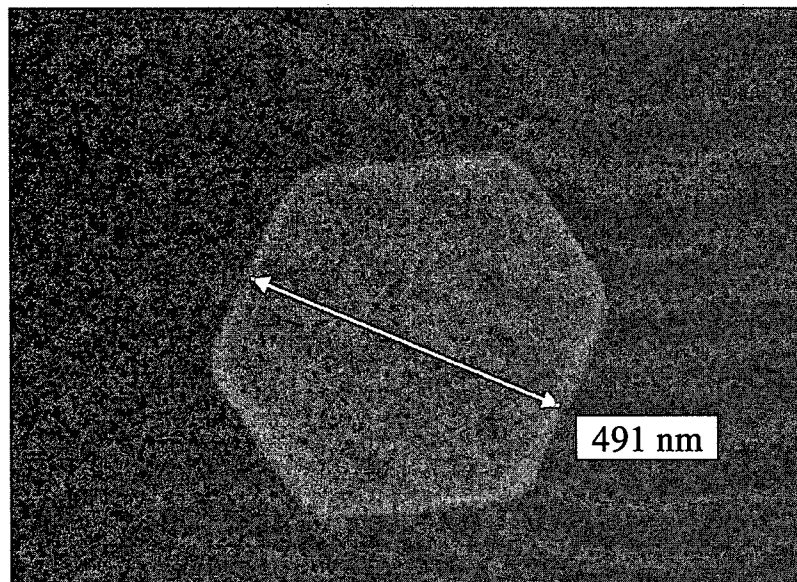
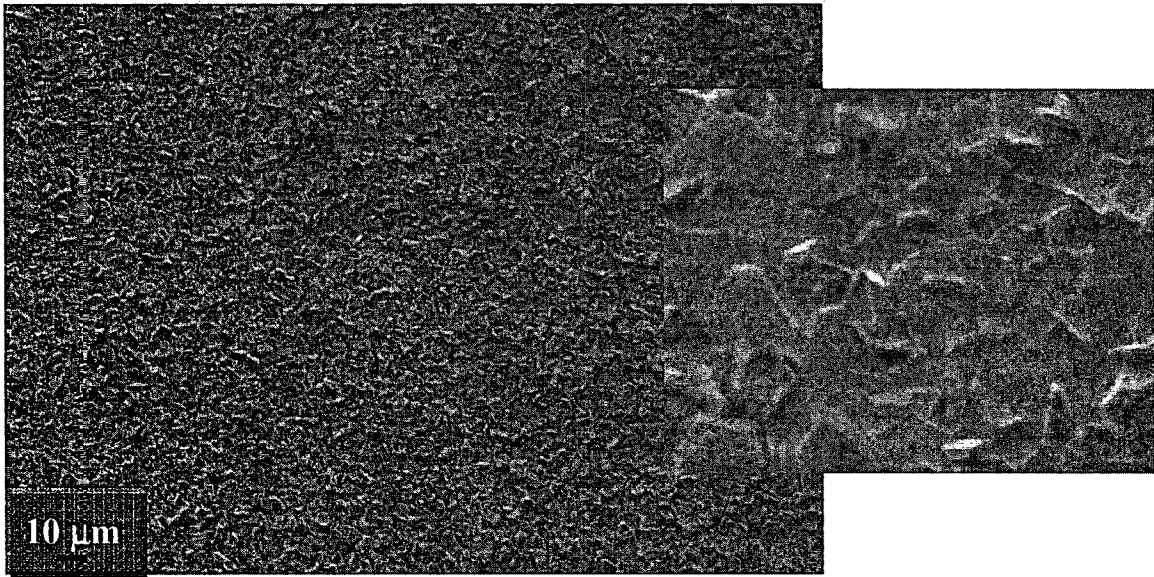


Figure 9

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Counts
(arbitrary)

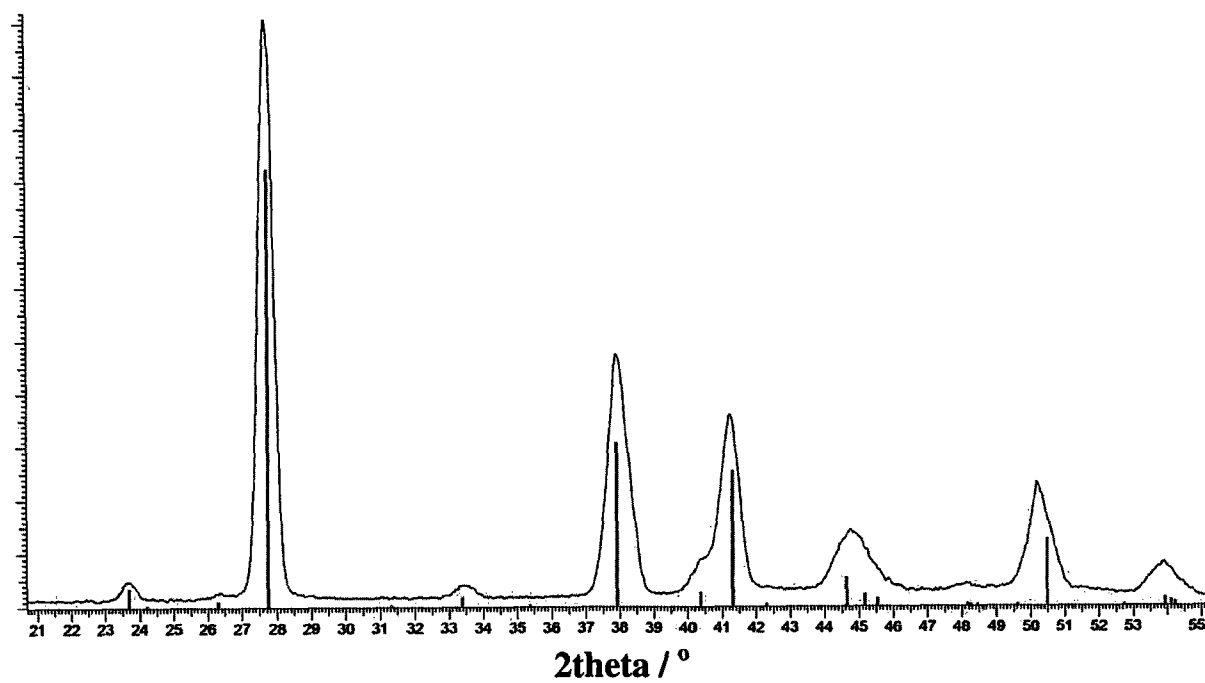
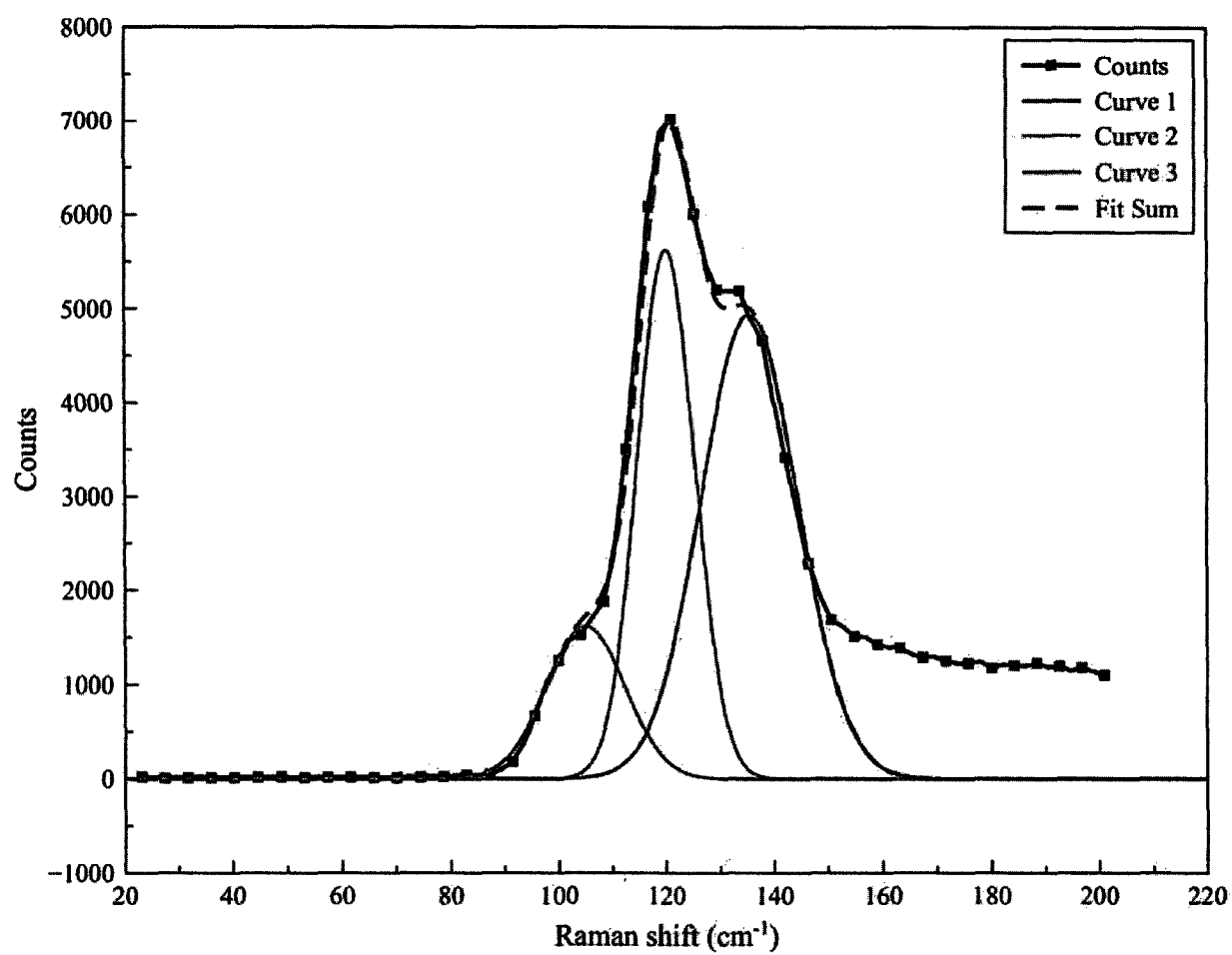


Figure 10

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**Figure 11**

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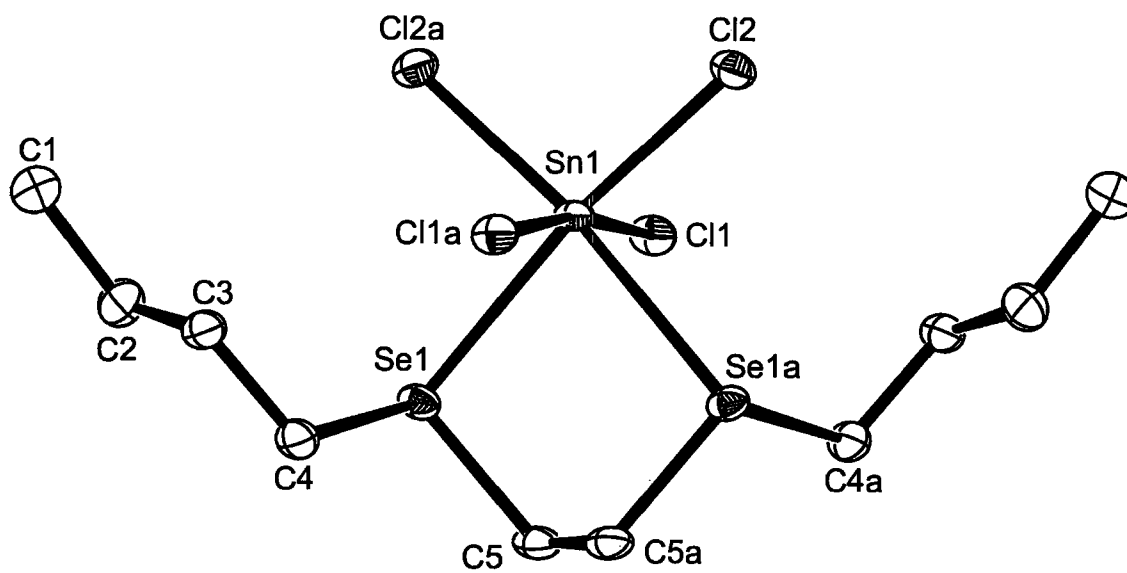
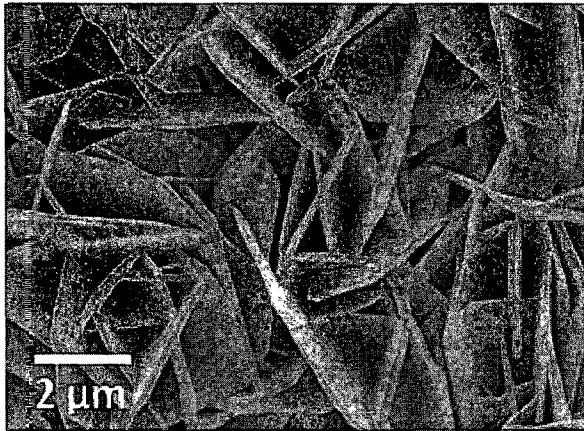
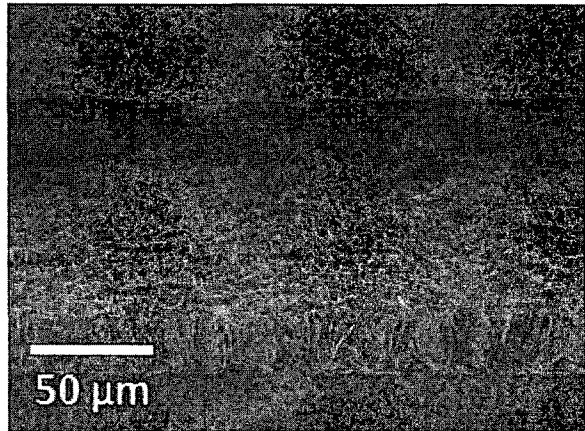


Figure 12

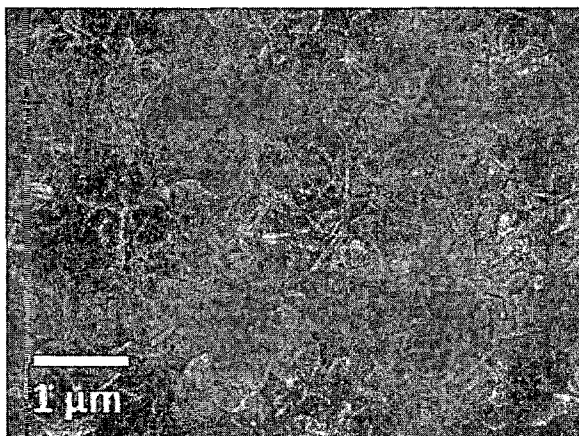
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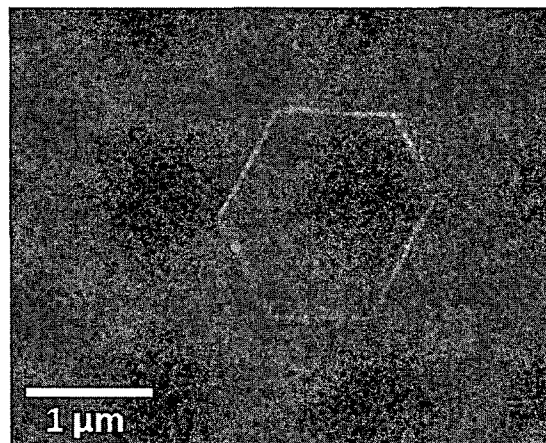
(a)



(b)



(c)



(d)

Figure 13

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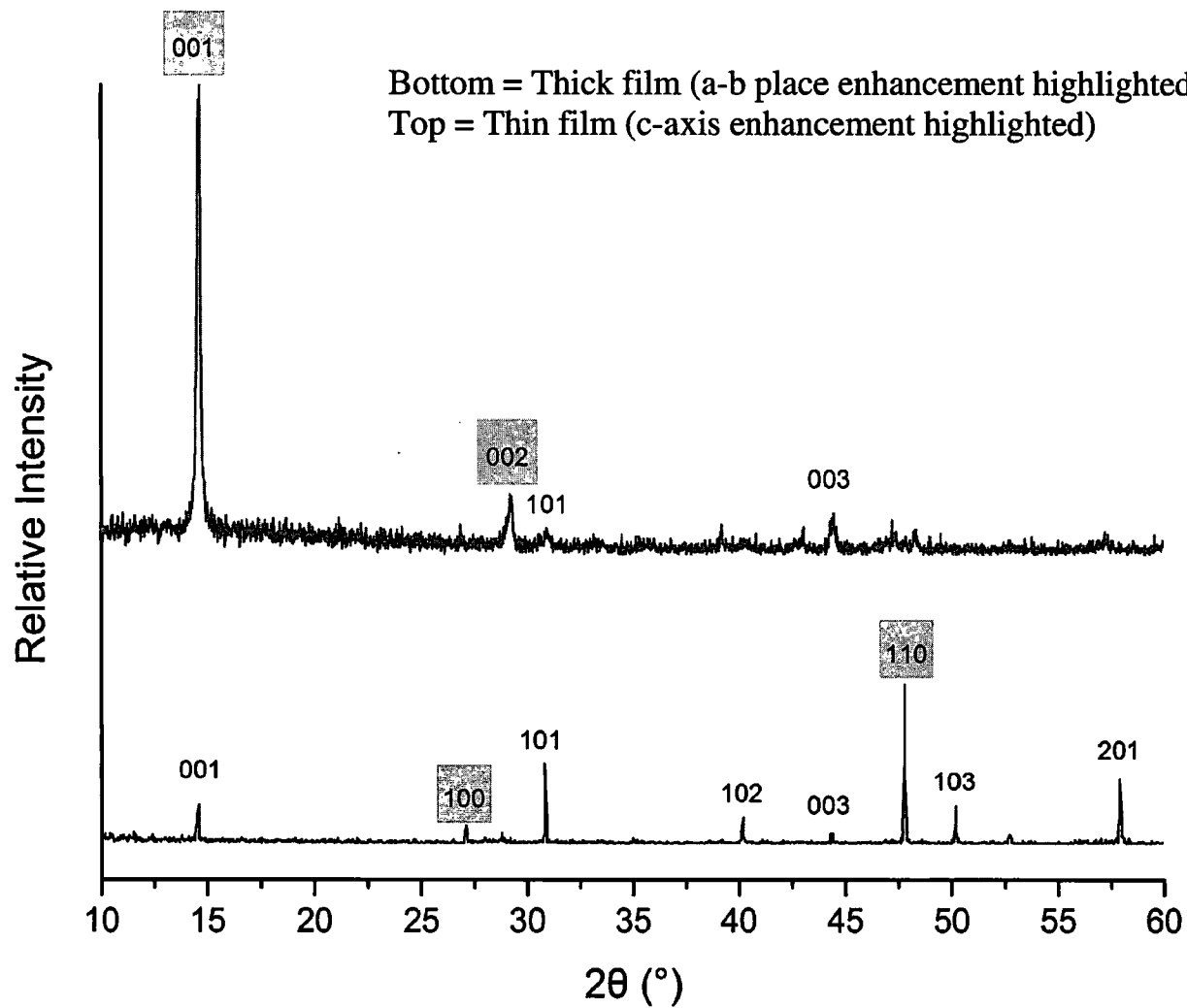
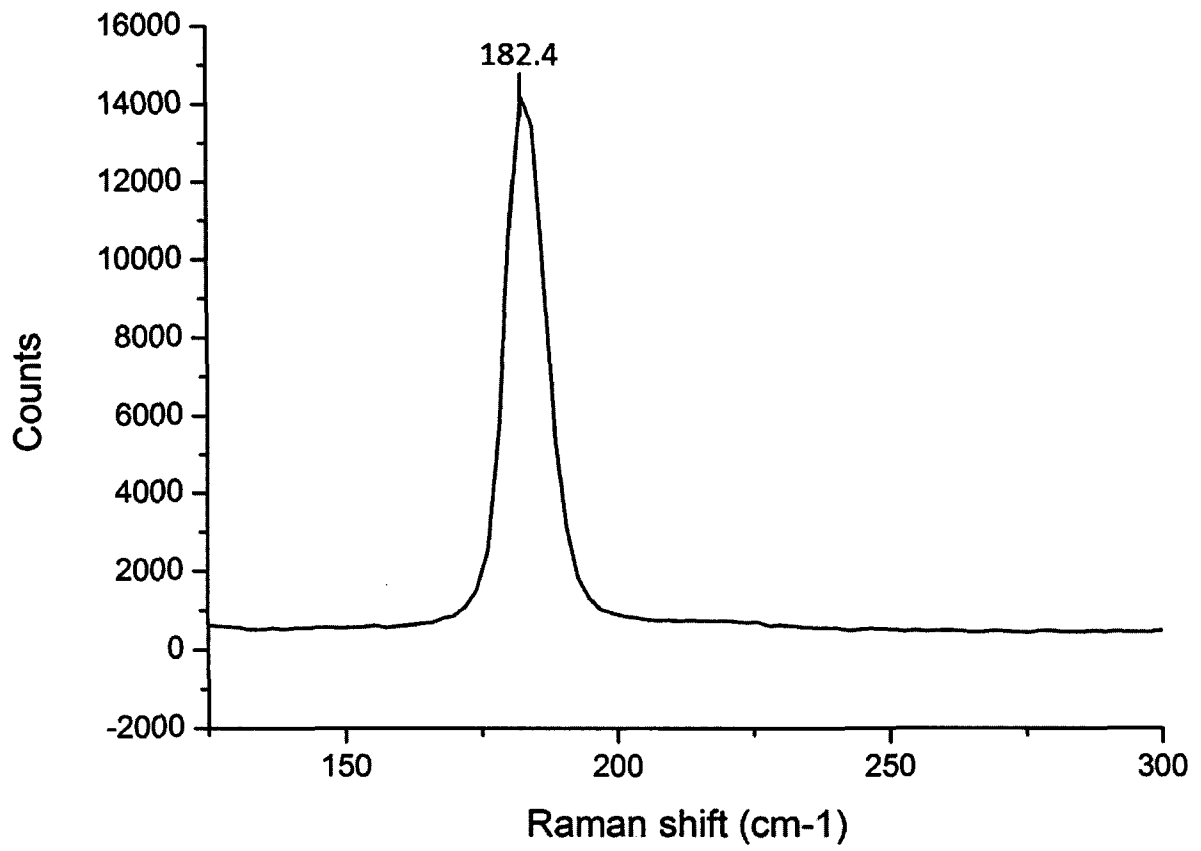
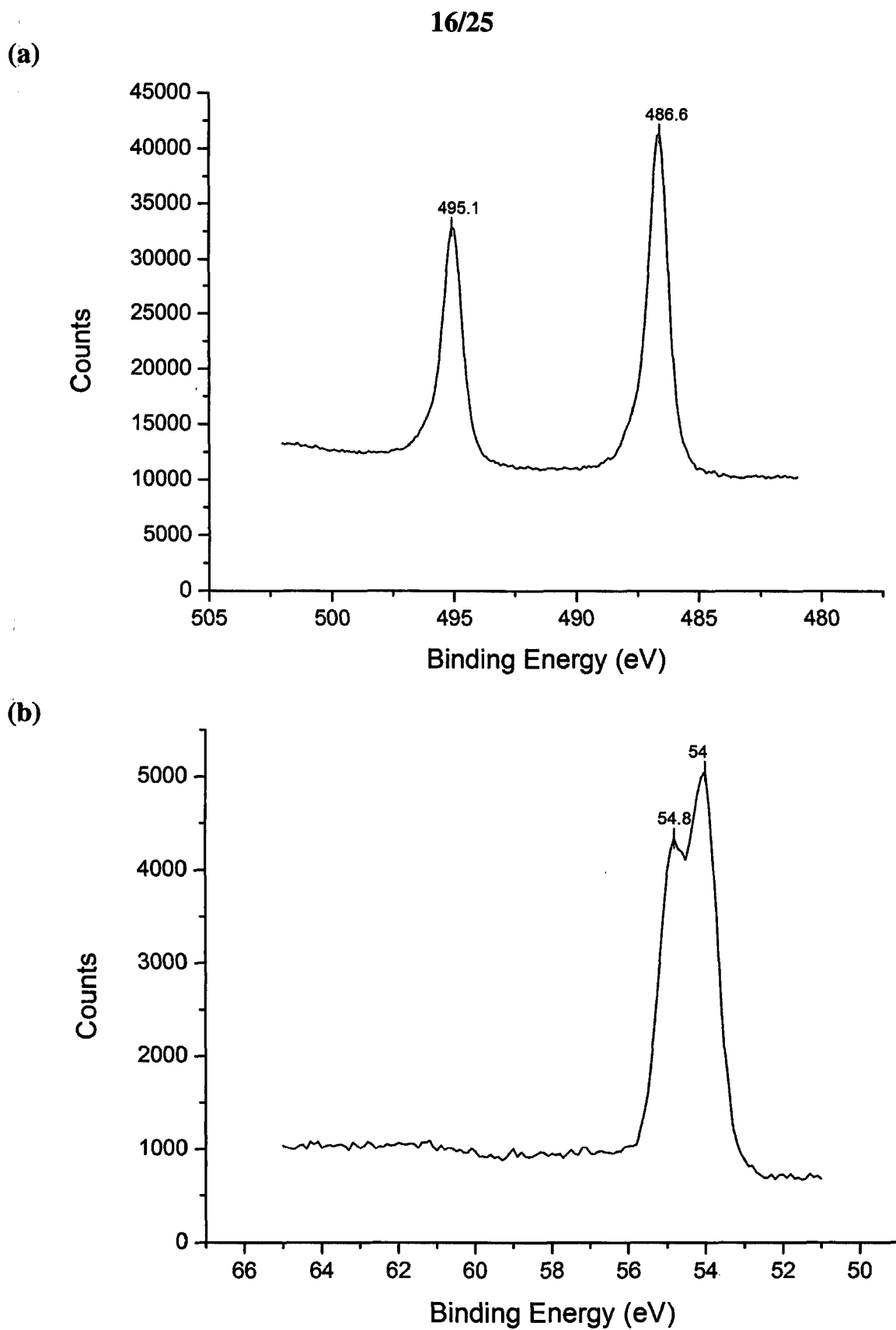


Figure 14

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**Figure 15**

**Figure 16**

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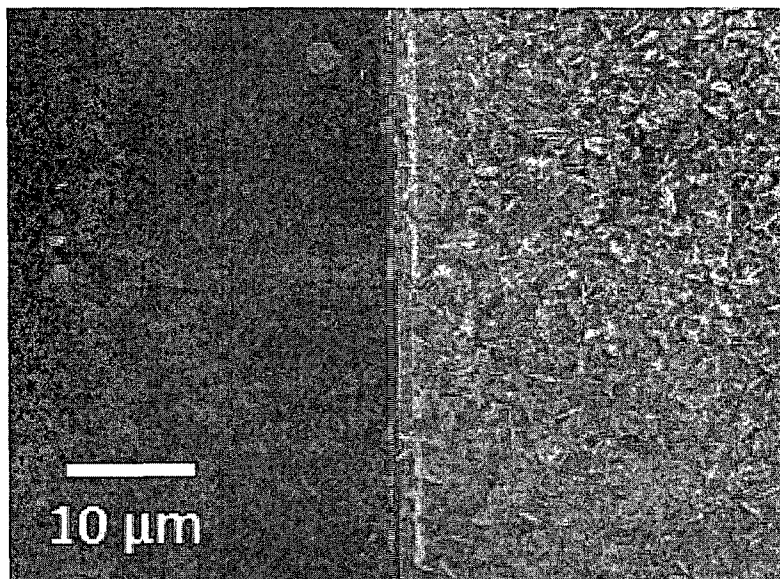


Figure 17

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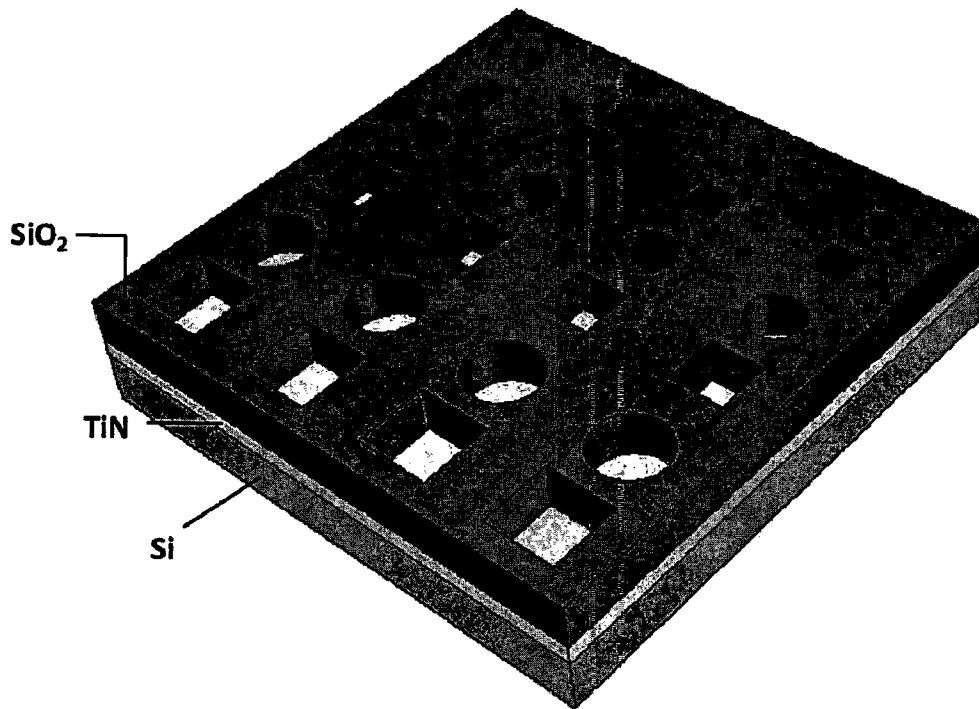
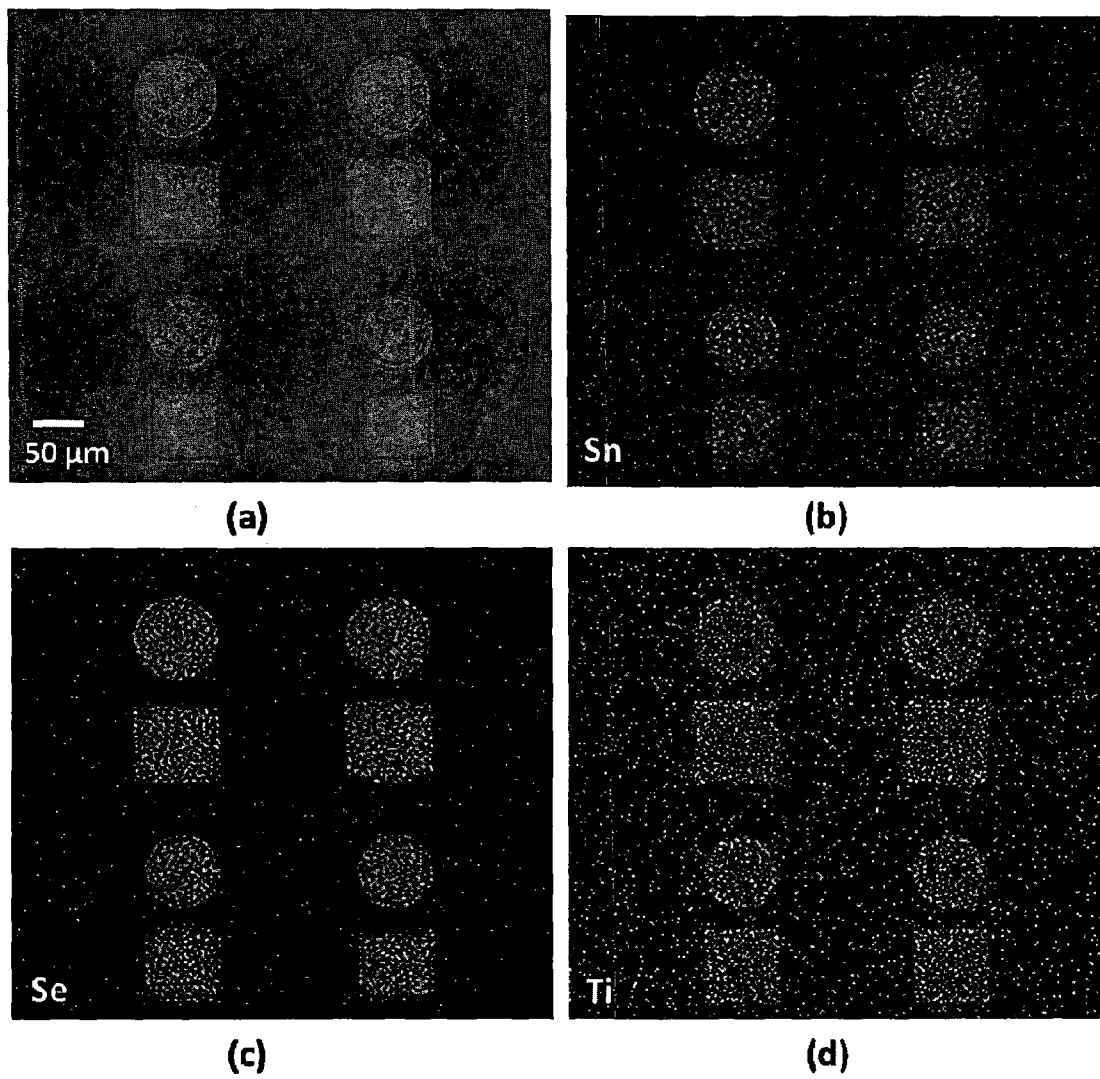


Figure 18

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**Figure 19**

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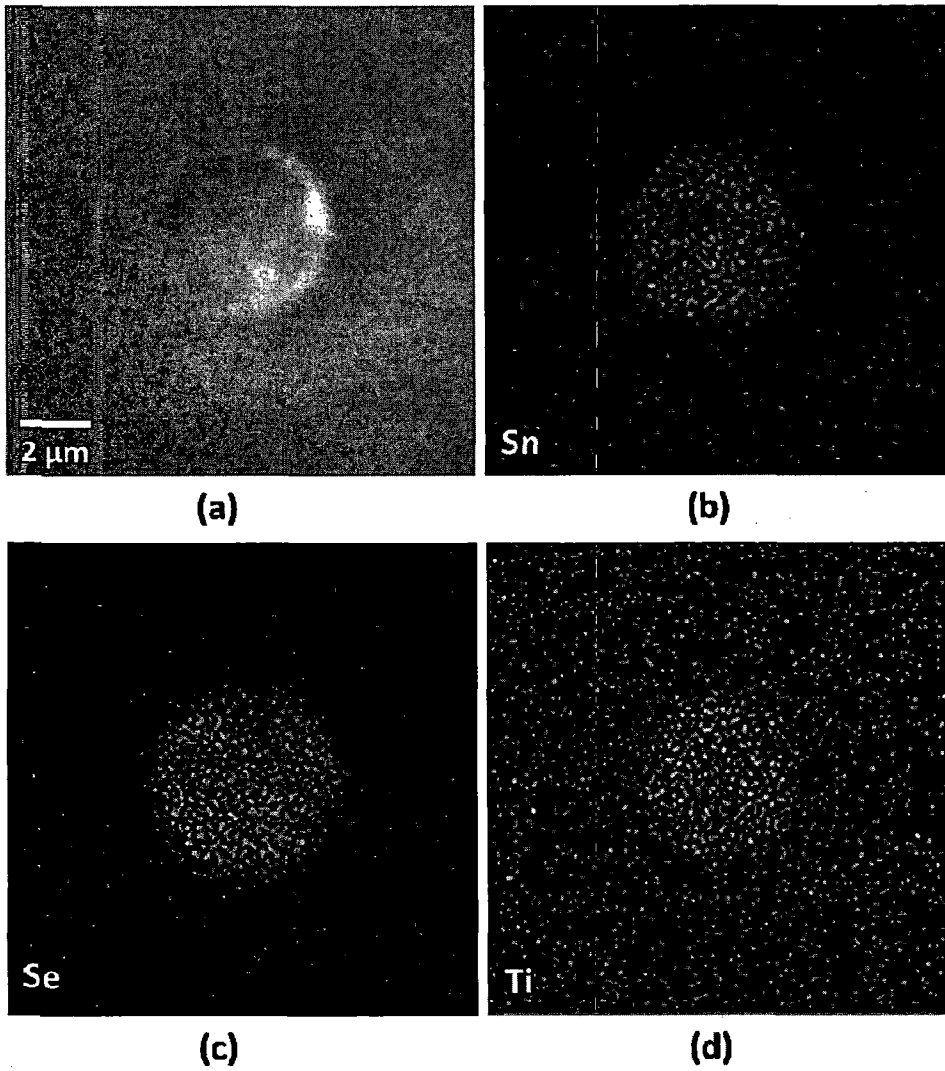


Figure 20

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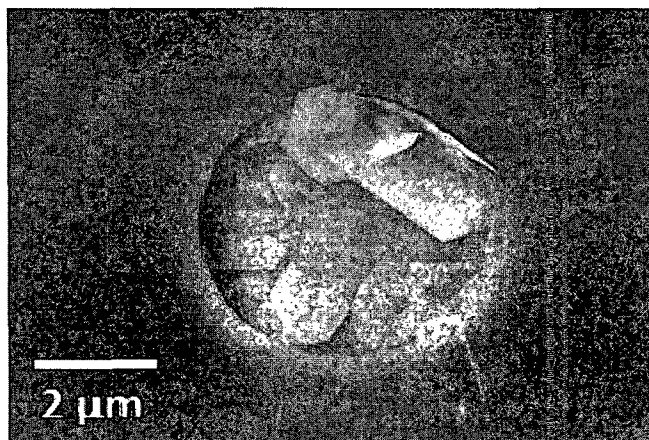


Figure 21

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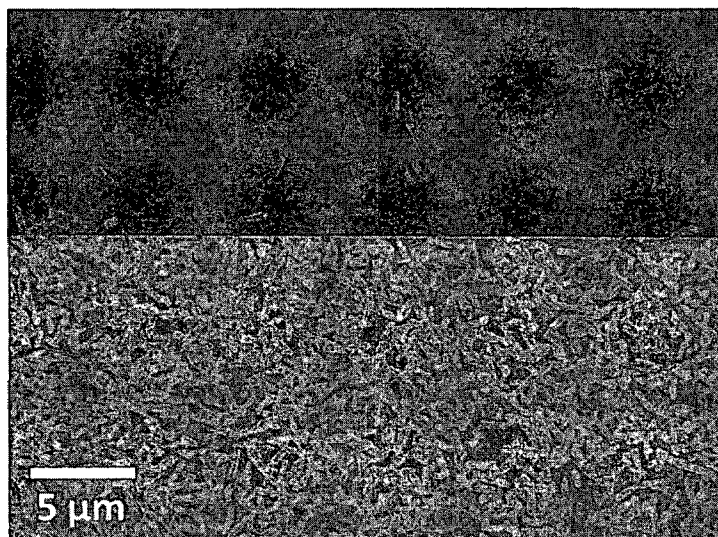


Figure 22

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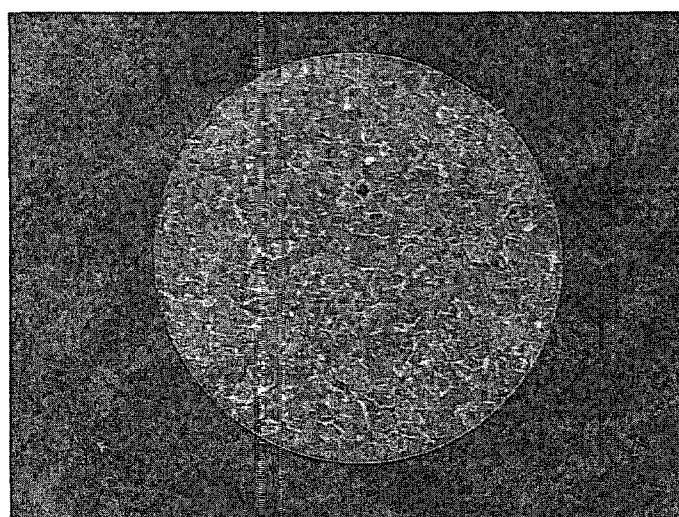
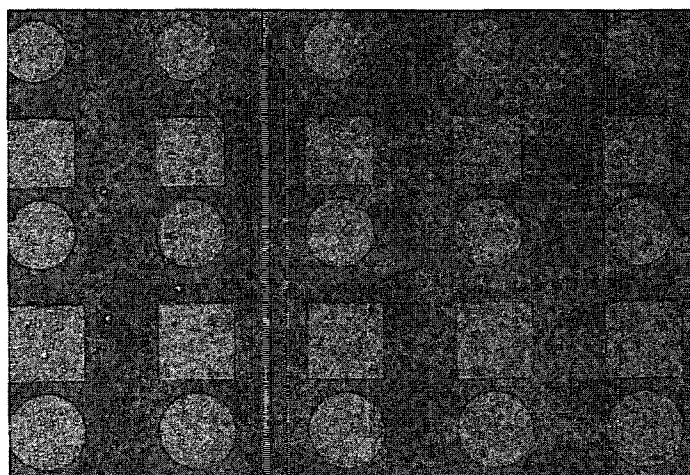


Figure 23

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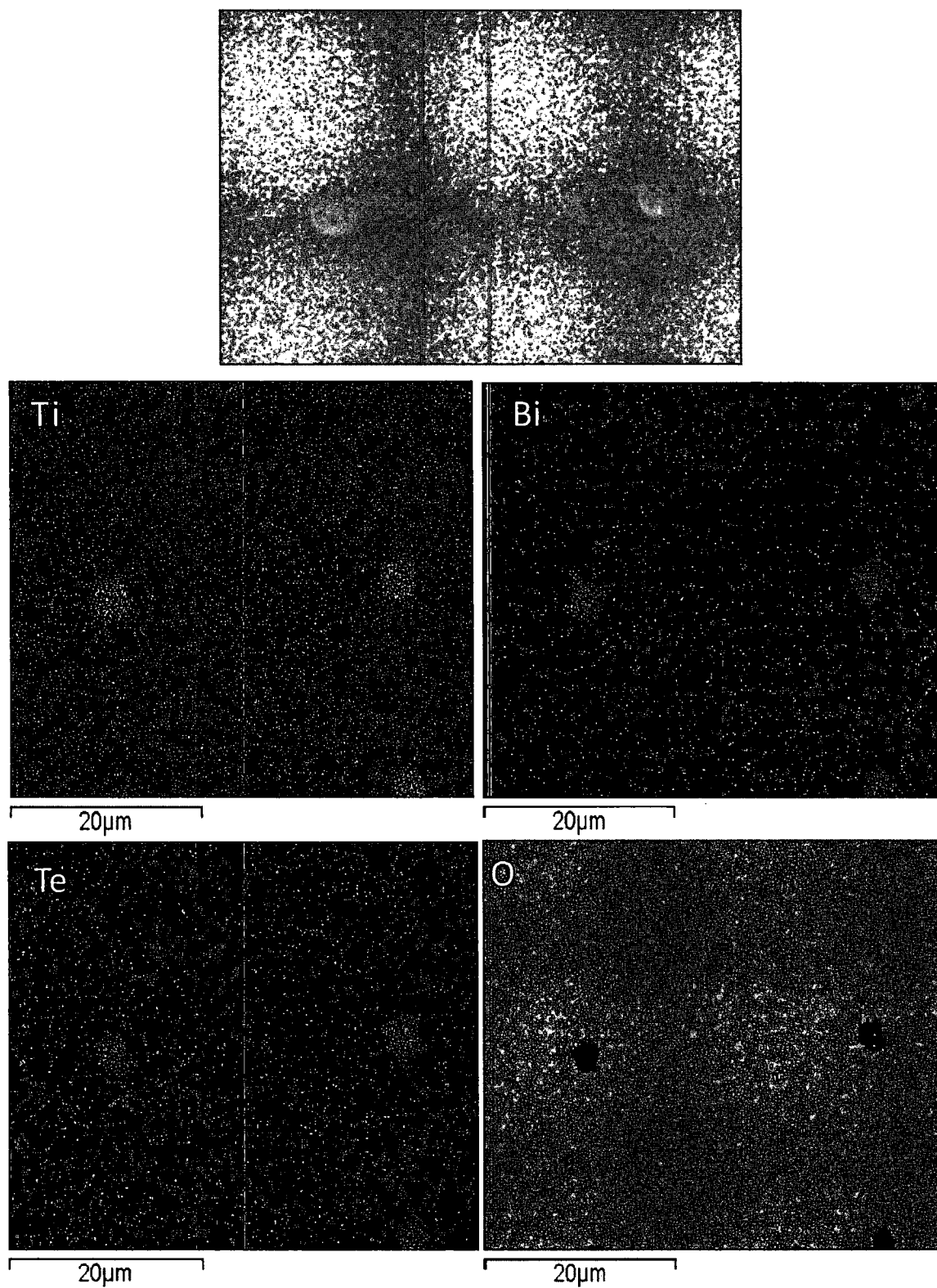


Figure 24

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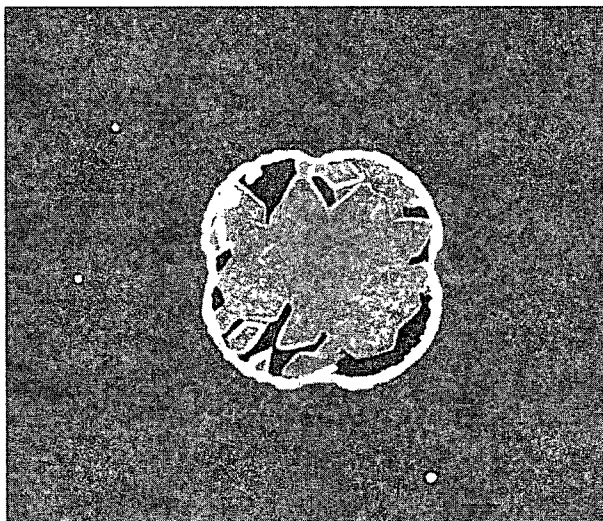


Figure 25

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/000307

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C16/30 H01L45/00 H01L21/02 C07C391/00 C07C395/00
C23C16/02 C23C16/04 C23C16/448

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C H01L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEVASON W ET AL: "The chemistry of the p-block elements with thioether, selenoether and telluroether ligands", DALTON TRANSACTIONS, vol. 40, no. 34, 27 June 2011 (2011-06-27), pages 8491-8506, XP055077975, RSC/Royal Society of Chemistry, Letchworth [GB] ISSN: 1477-9226, DOI: 10.1039/c1dt10317b page 8493 - page 8495 page 8498 page 8499 ----- -/-	1-17

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

11 September 2013

Date of mailing of the international search report

19/09/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Hoyer, Wolfgang

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/000307

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GURNANI C ET AL: "Synthesis, characterisation and structures of thio-, seleno- and telluro-ether complexes of gallium(III)", DALTON TRANSACTIONS, no. 44, 2 October 2008 (2008-10-02), pages 6274-6282, XP055077984, RSC/Royal Society of Chemistry, Letchworth [GB] ISSN: 1477-9226, DOI: 10.1039/b810005e table 1	1-11
X	----- GURNANI C ET AL: "Synthesis, characterisation and structures of thio-, seleno- and telluro-ether complexes of indium(III) halides", DALTON TRANSACTIONS, no. 9, 19 January 2009 (2009-01-19), pages 1611-1619, XP055078020, RSC/Royal Society of Chemistry, Letchworth [GB] ISSN: 1477-9226, DOI: 10.1039/b816148h page 1613	1-11
X	----- GENGE A R J ET AL: "Telluroether adducts of tin(IV) halides: synthesis, spectroscopy and structures", JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, vol. 23, 1997, pages 4549-4553, XP001191254, RSC/Royal Society of Chemistry, Letchworth [GB] ISSN: 1472-7773, DOI: 10.1039/A705829B page 4549	1-11
X	----- LEVASON W ET AL: "Synthesis and structural properties of the first bismuth(III) telluroether complex", JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, vol. 23, 1 November 2002 (2002-11-01), pages 4316-4317, XP055078039, RSC/Royal Society of Chemistry, Letchworth [GB] ISSN: 1472-7773, DOI: 10.1039/b209321a page 4316, left-hand column ----- -/--	1-11

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/000307

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BARTON A J ET AL: "Recent developments in thio-, seleno-, and telluro-ether ligand chemistry", HETEROATOM CHEMISTRY, vol. 13, no. 6, 28 August 2002 (2002-08-28), pages 550-560, XP055078245, John Wiley & Sons, Inc. [US] ISSN: 1098-1071, DOI: 10.1002/hc.10100 page 558, right-hand column -----	1-11
A	HOPE E G ET AL: "Synthesis, properties, and multinuclear NMR ($^{125}\text{Te}\{1\text{H}\}$, $^{13}\text{C}\{1\text{H}\}$, 1H) studies in di- and polytelluroether ligands", ORGANOMETALLICS, vol. 7, no. 1, January 1988 (1988-01), pages 78-83, XP055078617, ACS/American Chemical Society, Washington DC [US] ISSN: 0276-7333, DOI: 10.1021/om00091a015 the whole document -----	1-11
A	JONES C H W ET AL: "The preparation of di-t-butyl ditelluride and di-t-butyl telluride and the ^{125}Te NMR and Mössbauer spectra of some dialkyl tellurides and ditellurides", JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 255, no. 1, 11 October 1983 (1983-10-11), pages 61-70, XP055078347, Elsevier B.V., Amsterdam [NL] ISSN: 0022-328X, DOI: 10.1016/0022-328X(83)80173-9 the whole document -----	1-11
A	SINGH A K ET AL: "Recent Developments in the Ligand Chemistry of Tellurium", COORDINATION CHEMISTRY REVIEWS, vol. 209, no. 1, November 2000 (2000-11), pages 49-98, XP008144846, Elsevier Science, Amsterdam [NL] ISSN: 0010-8545, DOI: 10.1016/S0010-8545(99)00236-2 the whole document ----- -/--	1-17

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/000307

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	GEORGE K ET AL: "Telluroether and Selenoether Complexes as Single Source Reagents for Low Pressure Chemical Vapor Deposition of Crystalline Ga₂Te₃ and Ga₂Se₃ Thin Films", CHEMISTRY OF MATERIALS, vol. 25, no. 9, 18 March 2013 (2013-03-18) , pages 1829-1836, XP055078021, ISSN: 0897-4756, DOI: 10.1021/cm400382j the whole document -----	1-15