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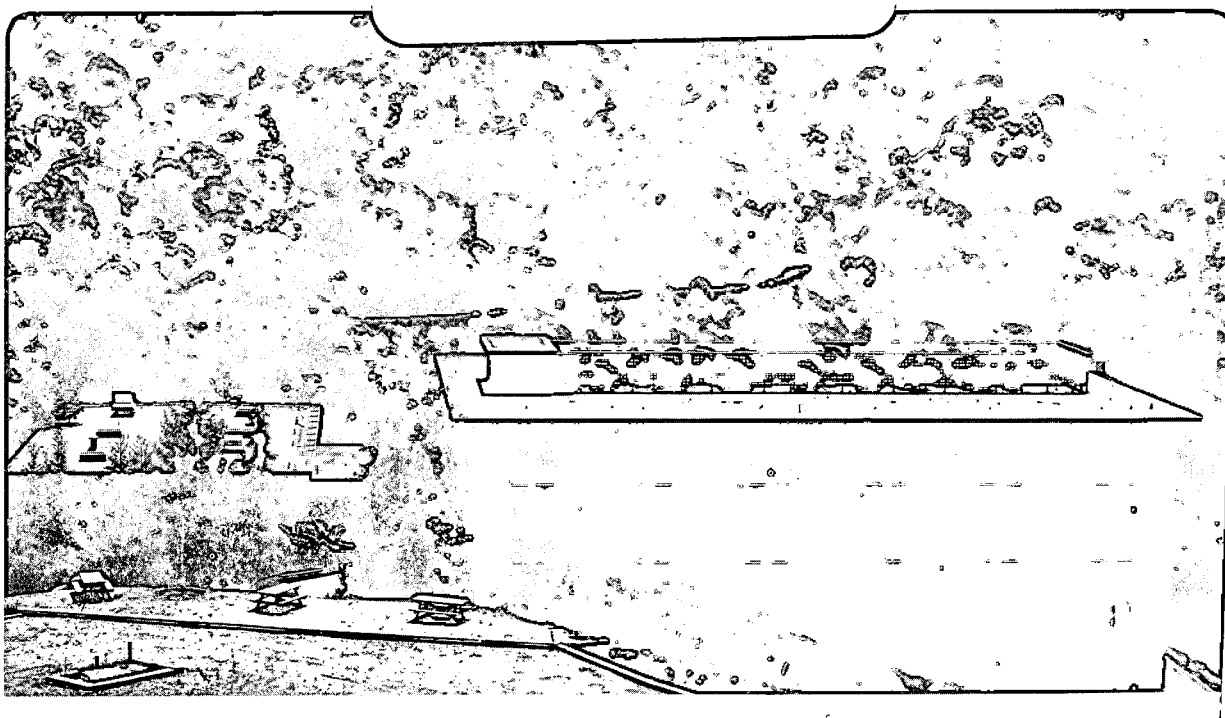

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J. ARNOLD and A.L. SELIGSON

Department of Chemistry
University of California
Berkeley, CA 94720

and

MATERIALS SCIENCES DIVISION
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

J.M. WALKER and E.D. BOURRET

MATERIALS SCIENCES DIVISION
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

P.J. BONASIA

Department of Chemistry
University of California
Berkeley, CA 94720

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Growth of II-VI Thin-Films from Single-Source Precursors Based on Sterically Encumbered Sitel Ligands

J. Arnold[•*], J.M.Walker[•], P.J.Bonasia[*], A.L. Seligson[•*] and E.D.Bourret[•]

[*] *Department of Chemistry, University of California, Berkeley CA 94720 and*

[•]*Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley CA 94720*

Abstract

We have developed a new route to MOCVD of II-VI compounds based on the use of novel single-source precursors in which the II-VI elements are combined at the molecular level in a single covalent compound. We have prepared and fully characterized a number of new derivatives of zinc, cadmium and mercury incorporating large, sterically demanding tellurolate ligands of general formula: $M(sitel)_2$ where sitel = $-TeSi(SiMe_3)_3$. The crystalline compounds are relatively volatile and are easily manipulated under nitrogen. Several of these compounds have been tested for their suitability as precursors in the MOCVD process. Clean pyrolysis reactions and deposition of thin films were achieved. The stoichiometry of the pyrolysis reaction has been determined by analysis of the reaction by-products.

1. Introduction

The use of molecular compounds as precursors to solid-state materials has burgeoned in recent years. These so called single-molecule precursors contain both elements of the binary compound to be formed, such that the elements are already covalently bonded. Advantages of these single-molecule precursors include: (i) their lower toxicity compared with presently employed dual-component systems (usually a metal alkyl and a hydride gas) (ii) simplification of the decomposition mechanisms (elimination of problems due to pre-reactions) and surface reactions, and (iii) the potential for precise control of film stoichiometry and growth rates.

For thin-film applications, volatile organometallic compounds are being developed as precursors to GaAs, GaP and numerous oxides, sulfides, and selenides [1]. For the Te containing materials, it has been shown [2-5] that aryltellurolates decompose to bulk metal tellurides as shown in eq 1. Due to the formation of tellurolate bridged oligomers, however, these compounds are non-volatile and are therefore, of little practical use in film growth.

$$[Hg(TePh)_2]_n \xrightarrow{\Delta} HgTe + TePh_2 \qquad (1)$$

Our recent studies of the molecular chemistry of Group II (12) compounds incorporating the large, sterically demanding sitel ligand, suggested that these compounds were ideal candidates for the preparation of II-VI films via chemical vapor deposition [6,7]. The compounds have the general formula $M(sitel)_2$. These compounds are easily manipulated under a nitrogen atmosphere. Here we describe the first examples of thin-film growth of II-VI materials incorporating tellurium via single-source precursors.

2. Experimental

2.1. Synthesis of the precursors

Preparation and purification of the crystalline tellurolate precursors, along with complete characterization has been described previously [6,7]. The compounds are slightly air-sensitive and were manipulated under an atmosphere of dry nitrogen. The mercury compound is slightly light sensitive and was handled in foil wrapped containers.

2.2. Deposition of II-VI compounds by CVD

The simple CVD reactor used to test the suitability of the new precursors for thin film deposition is shown in Figure 1. Axial temperature profiles measured inside the ampoule were conducted under specific growth conditions shown graphically in Figure 2. The cleaned substrates were placed in the ampoule at specified distances, as determined by the temperature profile, inside the two zone furnace. The precursor was loaded into a small quarzt boat which was introduced in the ampoule after thermal equilibration of the two zone furnace. The section of the ampoule containing the precursors was heated via heating tape and the temperature was maintained between 170 - 220 °C. Nitrogen was used as a carrier gas with flow rate varying from 100 to 200 sccm. Deposition experiments have been conducted at both atmospheric and reduced pressure. Reaction by-products were collected as condensates in a liquid nitrogen cooled trap and were fully characterized by ^{1}H and ^{13}C NMR spectroscopies, elemental analysis and electron impact (EI) mass spectroscopy.

3. Results and Discussion:

3.1. Synthesis of the precursors

The sitel imparts a number of desirable characteristics on its metal complexes; these include high thermal stability, solubility in non-reactive

hydrocarbon solvents, and sufficient volatility to render the compounds suitable for use as precursors to metal telluride thin-films via chemical vapor deposition (CVD). Use of the sitel ligand avoids many of the problems associated with the chemistry of group 12 metal chalcogenolates where formation of oligomeric networks supported by bridging chalcogenolate ligands is common [8-10]. Table I summarizes the physical characteristics of the precursors.

The crystalline compounds are easily manipulated under nitrogen and are volatile upon heating. Sublimation occurs below the melting point. Their structures have been investigated in solution, using ^{1}H, ^{125}Te, ^{199}Hg and ^{113}Cd NMR spectroscopy, and in the gas phase, by electron-impact mass spectroscopy. For all three metals, we observe only the monomeric compound in the gas phase, but in solution there is strong evidence for the existence of dimeric $[M(sitel)_2]_2$ species. For the zinc complex, further evidence for the latter structure was obtained from single crystal X-ray diffraction. This result is shown in Figure 3.

3.2. Deposition of II-VI compounds by CVD

Several compounds have been tested for their suitability as precursors in the MOCVD process. Table II summarizes various film growth conditions. Clean gas-phase pyrolysis reactions and deposition of thin films were observed for $Zn(sitel)_2$ and $Cd(sitel)_2$. Preliminary investigations of the deposition of HgTe and ZnSe films from analogous precursors are currently underway in our laboratory. Stoichiometry and composition of the films was determined by Rutherford Back-Scattering using 1.95 MeV He^+. The composition of these films was further confirmed by X-ray diffraction using a thin film detctor attachment on a Siemens D500 diffractometer.

<u>$Zn(sitel)_2$</u>

Deposition of ZnTe films from $Zn(sitel)_2$ has been obtained in the temperature range of 250 to 350 ºC at atmospheric pressure and 10 torr. Deposition occurred on the substrates as well as on the inner surface of the ampoule. The sublimation temperature of the precursor was approximately 210ºC at atmospheric pressure, and 180ºC at 10 torr. Stoichiometric films of ZnTe were obtained between 325 and 340 °C as confirmed by RBS measurements (figure 4(a)). At temperature below 325°C the films are Zn-rich while above 350°C, the ZnTe is decomposed as Zn metal appears to evaporate and pure Te deposits are obtained (figure 5). At atmospheric pressure conversion of the solid precursor to the gas phase is incomplete as judged by the observation of melted an subsequently decomposed starting materials within the quartz boat. At reduced pressure(c.a. 10 torr) the amount of material sublimed is greatly increased and the quartz crucible containing the precursors are most often empty and clean. Quartz and Si substrates were used to facilitate RBS measurements. ZnTe films were also grown on closely lattice-matched substrates, InAs and GaSb (0.69 and 0.08% mismatch respectively). Preliminary characterization analysis of the films grown on these substrates indicates interdiffusion between InAs and the ZnTe films.

<u>$Cd(sitel)_2$</u>

Stoichiometric films of CdTe have also been obtained by pyrolysis of $Cd(sitel)_2$ at temperatures between 280 and 350 °C at both atmospheric and reduced pressure (1.4 torr). Deposition was observed on the substrates as well as on the inner surface of the ampoule. The films obtained at atmospheric pressure were all slightly Te-rich. Residue in the crucible containing the precursor indicated that some decomposition and melting of the precursor occurred prior to sublimation and might have contributed to the loss of Cd. At 1.4 torr, a stoichiometric film was obtained at 290ºC, as determined by RBS

measurements (figure 4(b)). At pyrolysis temperatures >290 °C, the films became Cd-rich. As with the ZnTe precursor, the crucible containing the CdTe precursor was empty and clean after a run at reduced pressure.

The pyrolysis reaction was studied by analysis of the by-products collected at the reactor outlet which were confirmed to be $Te[Si(SiMe_3)_3]_2$ by comparison of the ^1H and ^{13}C NMR spectrum with authentic sample [6]. In all pyrolysis reactions $Te[Si(SiMe_3)_3]_2$ was the only tellurium containing product detected suggesting that deposition of the films occurs through a simple reaction pathway (eq 2-3):

<u>Sublimation</u>

$$\{M[TeSi(SiMe_3)_3]_2\}_2 \text{ (solid)} \rightarrow 2\,\{M[TeSi(SiMe_3)_3]_2\} \text{ (gas)} \quad (2)$$

(M=Zn or Cd)

<u>Pyrolysis</u>

$$M[TeSi(SiMe_3)_3]_2 \rightarrow (MTe)_n + Te[Si(SiMe_3)_3]_2 \quad (3)$$

The exact mechanism of this pyrolysis is currently under investigation.

These preliminary results are very promising as they show that metal organic CVD using our tellurium-based single-molecule precursor compounds can lead to the desired II-VI semiconducting thin films. Further tests using these new precursors in a specifically designed OMVPE reactor, that will allow in-situ cleaning of the substrates and proper control of the growth conditions, are underway.

4. Conclusions

We have demonstrated that a new class of single-molecule precursors of general formula: $\{M[TeSi(SiMe_3)_3]_2\}_2$ where M = Zn, Cd or Hg, sublime cleanly

on heating to produce monomeric species that pyrolyze cleanly with deposition of thin films. The films are stoichiometric for well-defined temperatures.

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Figure captions.

Figure 1. CVD reactor design.

Figure 2. Representative axial temperature profiles measured inside the ampoule at atmospheric (+) and reduced pressure, 1.4 torr (o) for CVD experiments.

Figure 3. Computer generated representation of the solid-state structure of $\{Zn[TeSi(SiMe_3)_3]_2\}_2$ as determined by single crystal X-ray diffraction.

Figure 4. RBS spectrum of (a) ZnTe deposited on a quartz substrate under atmospheric pressure and (b) CdTe deposited on a Si substrate at 1.4 torr.

Figure 5. Stoichiometry of ZnTe as determined by RBS for various growth temperatures.

Table I:

Characteristics of the new single-molecule precursors.

Precursor	Physical properties	Melting point (ºC)
$Zn(sitel)_2$	Solid Bright yellow crystals Oxygen sensitive	208-213
$Cd(sitel)_2$	Solid Bright yellow crystals Oxygen sensitive	210-220
$Hg(sitel)_2$	Solid Pale green needles Light sensitive	128-130

Table II:
List of deposition conditions.

Precursor	Deposition temperature	Pressure/flow	Substrate used
$Zn(sitel)_2$	250 to 350 ºC	1 atm N_2 = 100sccm	quartz silicon InAs
$Zn(sitel)_2$	250 to 350 ºC	10 torr N_2 = 100sccm	InAs GaSb
$Cd(sitel)_2$	235 to 345 ºC	1 atm N_2 = 200sccm	silicon
$Cd(sitel)_2$	280 to 345 ºC	1.4 torr N_2 = 100sccm	silicon

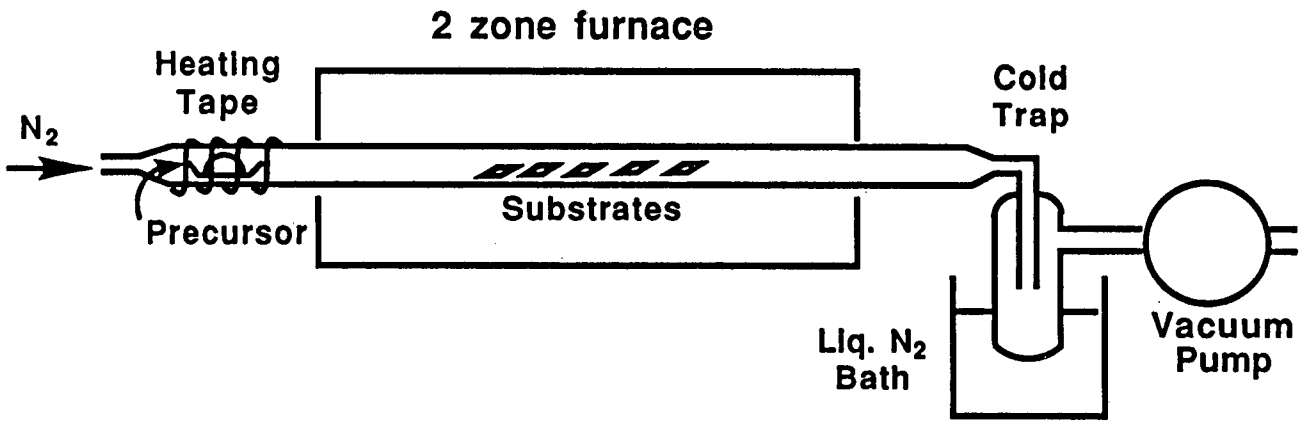

2 zone furnace
Heating Tape
N_2
Precursor
Substrates
Cold Trap
Liq. N_2 Bath
Vacuum Pump

Figure 1.

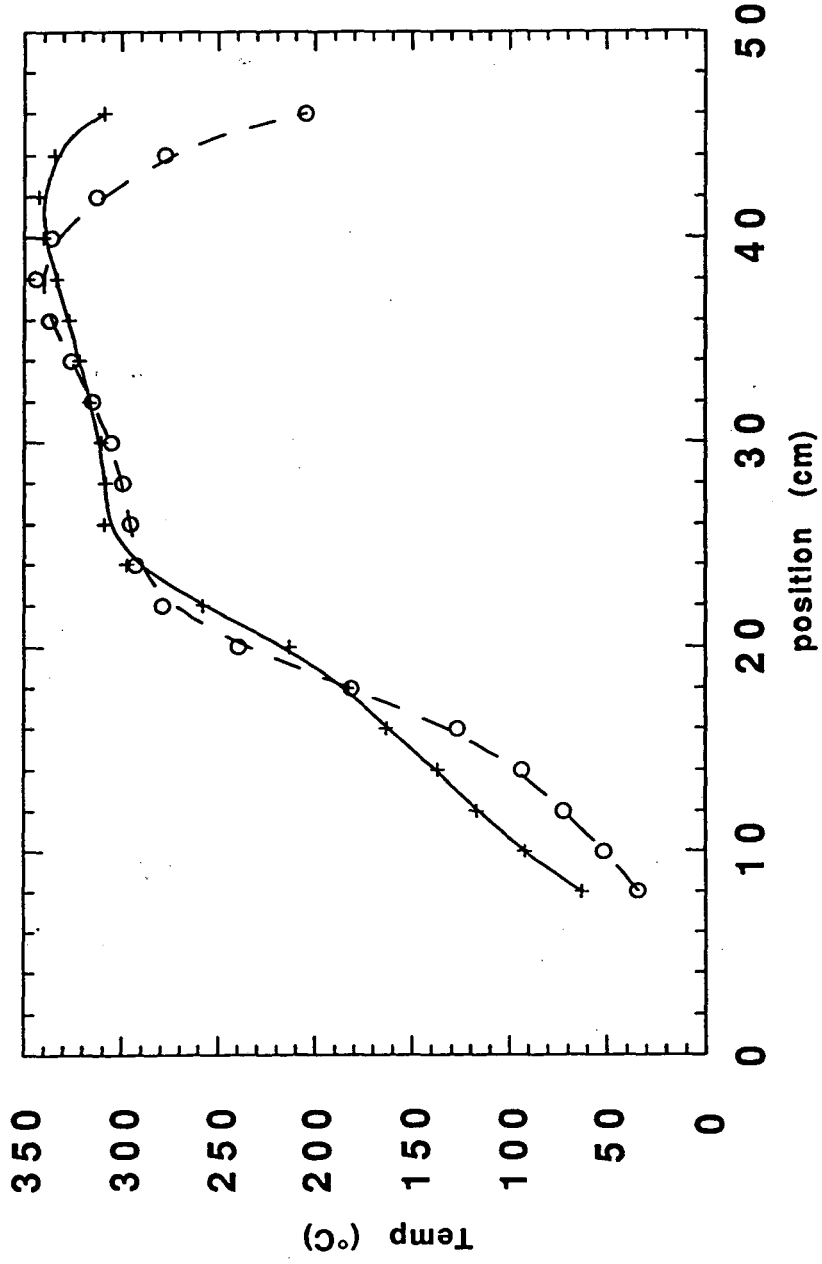


Figure 2.

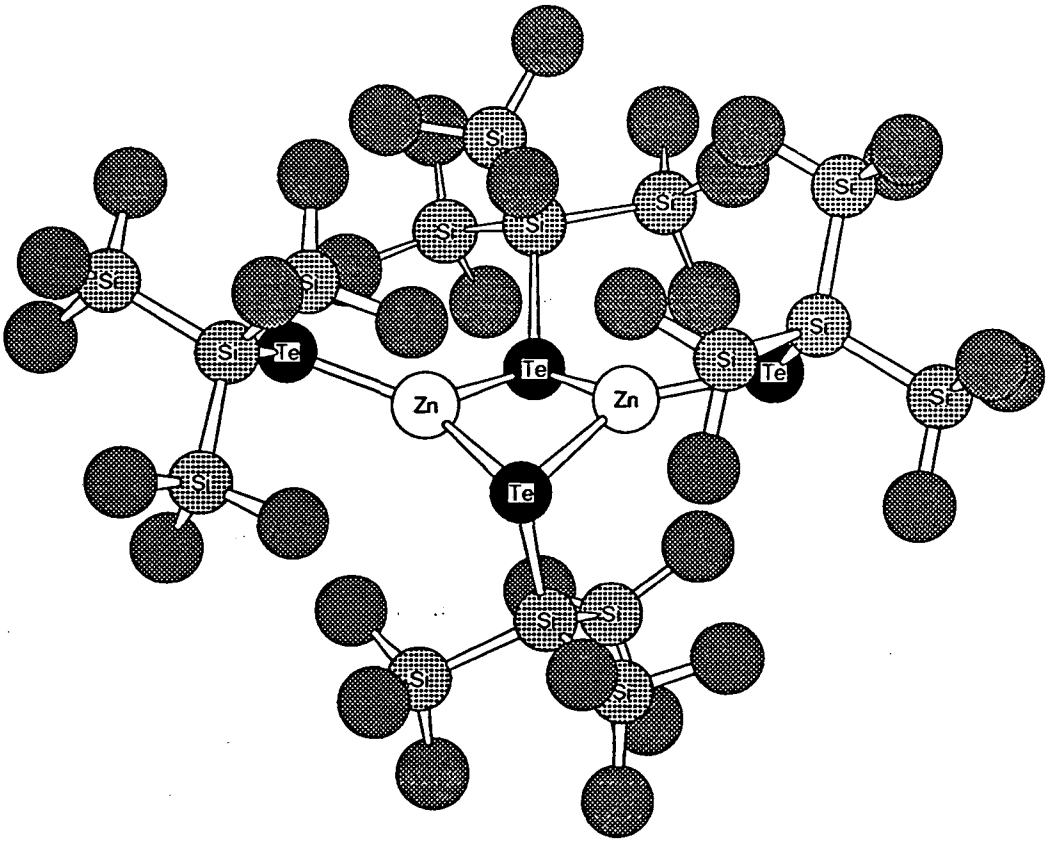
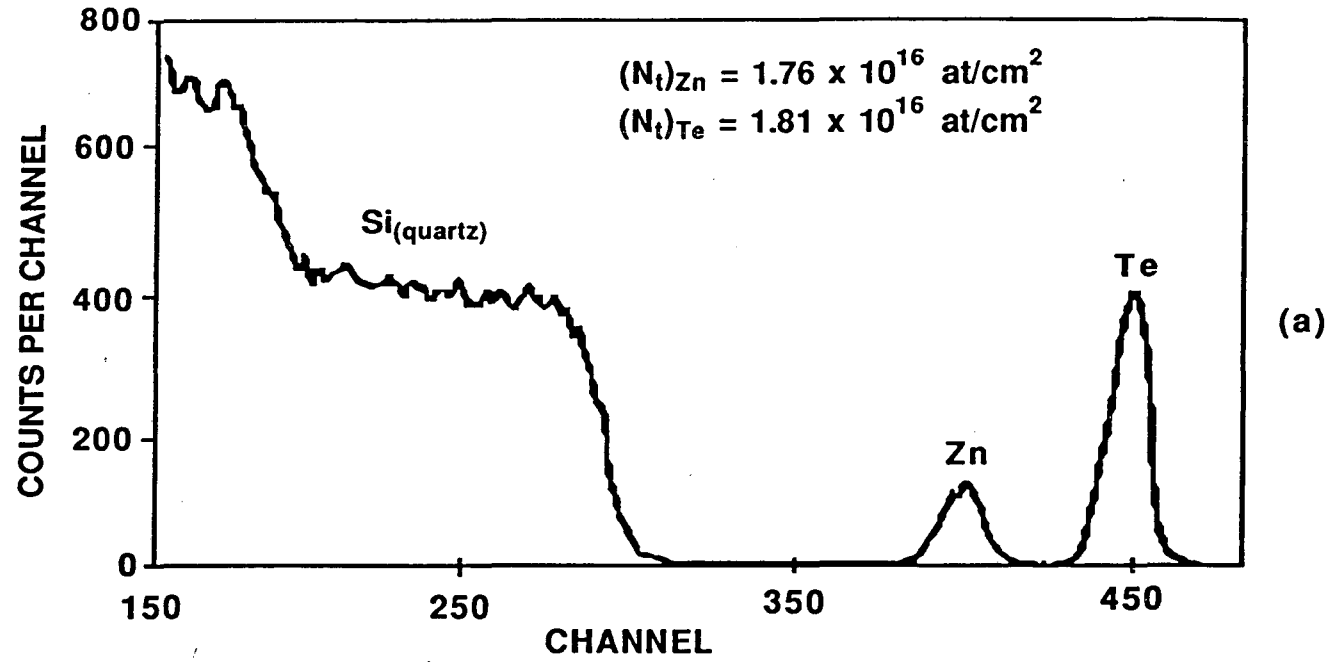


Figure 3.


800
600
400
200
0
COUNTS PER CHANNEL
$(N_t)_{Zn}$ = 1.76 x 10^{16} at/cm^2
$(N_t)_{Te}$ = 1.81 x 10^{16} at/cm^2
$Si_{(quartz)}$
Te
Zn
150
250
350
450
CHANNEL
(a)

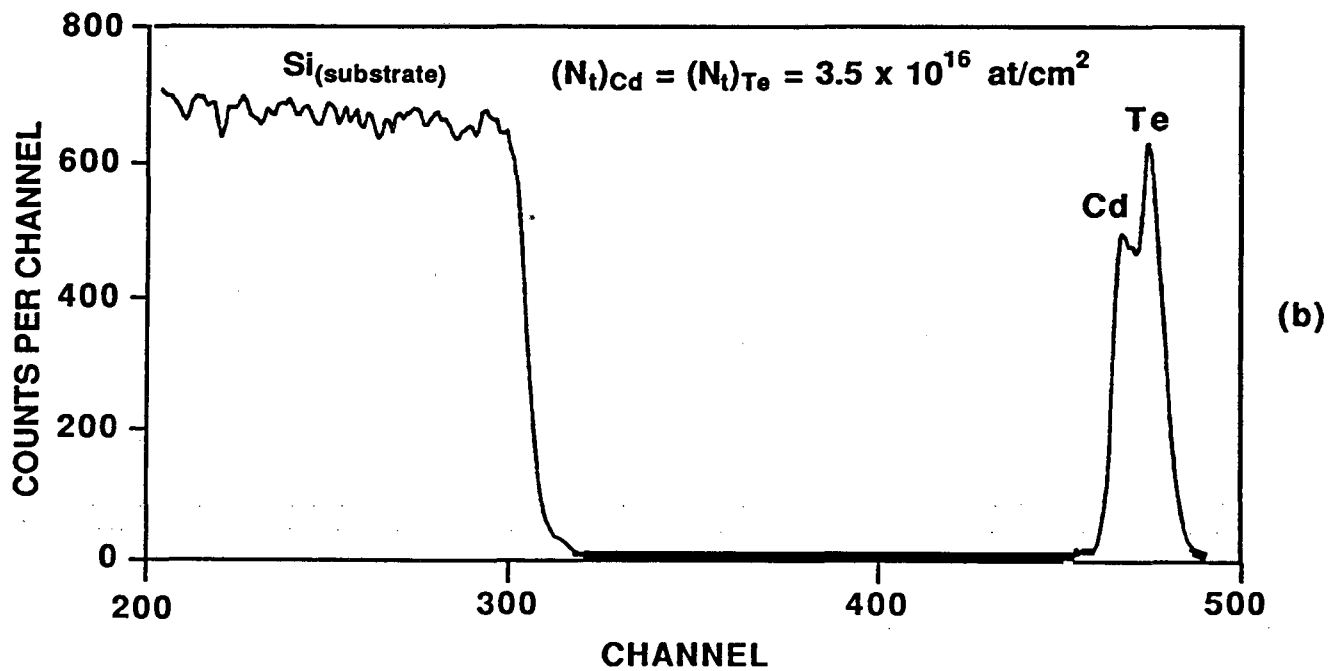

800
600
400
200
0
COUNTS PER CHANNEL
$Si_{(substrate)}$
$(N_t)_{Cd} = (N_t)_{Te}$ = 3.5 x 10^{16} at/cm^2
Te
Cd
200
300
400
500
CHANNEL
(b)

Figure 4.

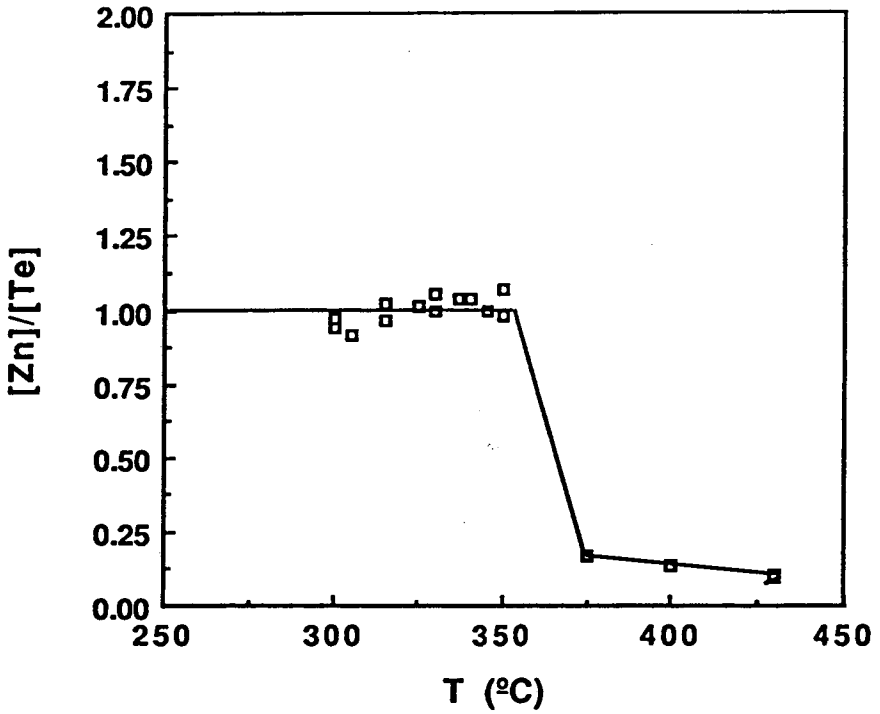


Figure 5.

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