Deposition of thin films of CdSe or ZnSe by MOCVD using simple air stable precursors

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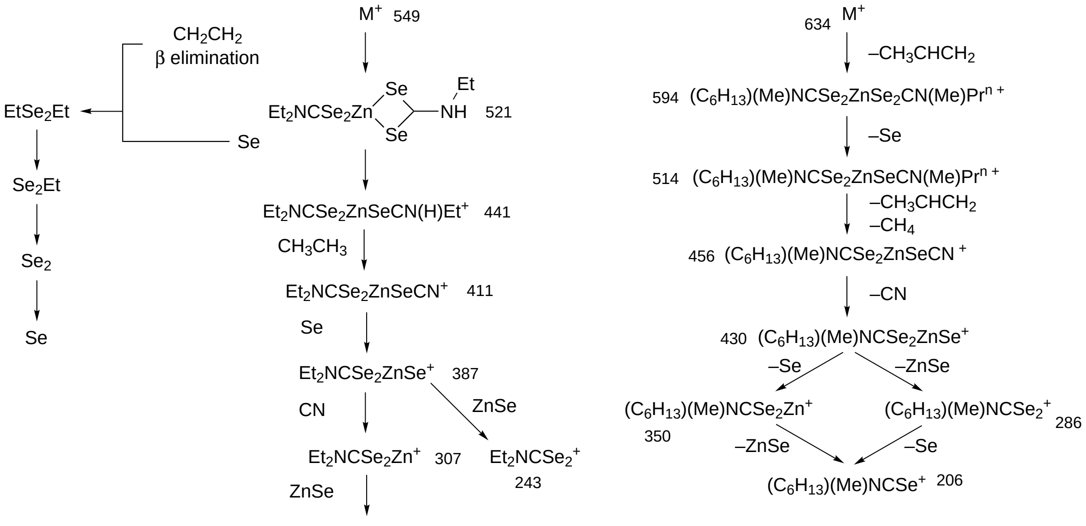
The air-stable bis-complexes of methyl (*n*-hexyl)diselenocarbamate with cadmium or zinc have been shown to be effective precursors for the deposition of the metal chalcogenides by MOCVD; studies of their thermal decomposition mechanism provide possible explanations as to why these complexes are effective whilst simpler ones are not.

Cadmium and zinc selenide are compound semiconductors with optoelectronic and/or photovoltaic applications.[1] There are many reports in the literature of attempts to develop effective single-source precursors for the deposition of such materials by MOCVD (metal organic chemical vapour deposition).[1,2] We have developed one such approach using dithio-[3,4] monothio-[5] and diseleno-carbamates.[6,7] One striking observation has concerned differences between the behavior of the simple bis-diethyldithio- and bis-diethyldiseleno-carbamates of zinc and cadmium. The bis-diethyldithiocarbamates are effective precursors for materials such as CdS and films of good quality can be deposited.[4,8] However, attempts to use the related selenium compounds lead to films of elemental selenium or metal selenide films heavily contaminated with elemental selenium.[9] In efforts to increase the volatility of this family of precursors we have used bulkier substituents on the amine parent of the carbamate.[4] Here, we report that we have now discovered that some of these air stable compounds are effective precursors for the deposition of the metal selenides. This unexpected result can be understood in terms of quite subtle changes in the mechanism of thermal decomposition of the complexes.

Fig. 1 Typical thin film of CdSe on glass from $[Cd\{Se_2CNMe(C_6H_{13})\}_2]$, T_{source} = 250 °C, T_{growth} = 450 °C, 2 h growth run; bar is 10 μm

The complexes used as precursors, bis[methyl(*n*-hexyl)-diselenocarbamato]-zinc **1** or -cadmium **2**, are air stable solids melting at 151–152 and 130–132 °C respectively.‡ Thin films of CdSe and ZnSe were deposited by low pressure (LP)–MOCVD as described previously.[10] Films were deposited on glass microscope slides and growth runs were typically for times between 30 min and 2 h. After 2 h, thick, *ca.* 3 μm films were deposited (T_{source} = 200–250 °C, T_{growth} = 400–450 °C). Growth rates were *ca.* 1 μh^{-1} for ZnSe and 1.5 μh^{-1} for CdSe. The films formed were all of substantial thickness, adherent and fully dense; Fig. 1 shows a typical electron micrograph. The surface of all these films tended to be featureless. Cross-sectional microscopy of thicker samples revealed a columnar structure.§ EDAX analysis results of the selenide films gave a metal : chalcogenide ratio approximating 1 : 1; in the case of zinc there appeared to be a significant, but small, oxygen content (*ca.* 3% of total). The optical band gaps of the as-



Scheme 1 Plausible decomposition mechanism for $[Zn(Se_2CNEt_2)_2]$ and $[Zn\{Se_2CNMe(C_6H_{13})\}_2]$ combining the steps observed from GC–MS and EI$^+$ studies of the precursors

deposited films were estimated by using the direct band gap method (from plots of absorbance[2] *vs.* energy) as 1.70 eV for CdSe and 2.58 eV for ZnSe (literature 1.74 and 2.58 eV). The films were further characterized by X-ray diffraction.¶

Compounds **1**, **2** and the analogous bis-diethyldiselenocarbamate were studied by pyrolysis GC–MS (pyrolysis temperature of 370 °C) and EIMS to develop plausible decomposition pathways/mechanisms for both sets of precursors.‖ These methods give valuable information concerning probable stable decomposition products and the results of these studies are summarized in Scheme 1. The gas chromatogram of the bis-diethyldiselenocarbamates for both cadmium and zinc shows the formation of a number of organoselenide products of which the most abundant is diethyl diselenide, EtSe$_2$Et. At the higher GC-column temperature (*ca.* 240 °C) elemental selenium fragments Se$_n$ (n = 1–7) are observed which indicates that clusters of selenium are being formed on the pyrolysis of the precursor. These species may be responsible for the formation of selenium films during MOCVD. The selenium clusters were probably formed *via* an intermediate organoselenium complex on the column, EtSe$_2$Et is a likely candidate as the mass spectrum of EtSe$_2$Et shows it to dissociate to elemental selenium. In contrast to the diethyl derivative, the GC–MS traces of **1** and **2** show no evidence for the formation of selenium clusters, or the volatile organoselenium compound EtSe$_2$Et.[11]

We believe that by changing the alkyl groups on the parent amine of the diselenocarbamates from the symmetric diethyl to the asymmetric methyl(n-hexyl) derivative, the formation of diethyl diselenide is hindered and thus the deposition of selenium during film growth is inhibited. This subtle change results in the successful deposition of the ZnSe and CdSe from **1** and **2**.

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Notes and References

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‡ The compounds were prepared by adaptations of the literature methods[3,4] for metal bis-dithiocarbamates and have been fully characterized by: NMR, mass spectrometry, microanalysis and IR spectroscopy.

§ For the purposes of analysis, samples were carbon coated and electron microscopy/EDAX was performed on a JEOL Superprobe 733 microscope.

¶ X-Ray diffraction of the films gave intense peaks with d values (% relative intensity, *hkl*) of 3.26 Å (100, 111), 2.00 Å (20, 220) and 1.71 Å (12, 311) for ZnSe (corresponding to cubic zinc selenide with a preferred orientation of 111; 3.27 (100), 2.00 (70), 1.71 Å (44) {ASTMS}) and 3.72 Å (21, 100), 3.51 Å (100, 002), 3.28 Å (18, 101), 2.54 Å (14, 102) 2.15 Å (15, 110), 1.98 Å (36, 103), 1.83 Å (11, 112), 1.45 (4, 203) Å for CdSe (corresponding to hexagonal CdSe with a preferred orientation of 001; 3.72 (100), 3.51 (70), 3.29 (75), 2.55 (36), 2.15 (85), 1.98 (70), 1.83 (51), 1.45 Å (20) {ASTMS}).

‖ EI-MS: a micromass AutoSpec-Q, using Micromass OPUS software was used. An electron impact energy of 70 eV at 10^{-7} Torr was used to initiate mass fragmentation. GC-MS: analysis of the samples was carried out using a Hewlett Packard Series II Gas/Liquid chromatograph linked to a JEOL JMS AX505W mass spectrometer. The chromatography conditions were as follows: column BP1 (supplied by SGE). Bonded phase methyl siloxane, length of 25 m, inner diameter of 0.22 mm, Phase thickness 0.25 µm. The temperature program employed for analysis was, initial temperature 30 °C, initial time 2 min, 8 °C min^{-1} to 100 °C (first ramp rate), 12 °C min^{-1} (second ramp rate), final temperature 280 °C. The pyrolysis injector temperature was 370 °C. Carrier gas helium pressure of 12 psi, flow 1 cm^3 min^{-1}. MS settings were a 3 kV accelerating voltage, 100 µA beam current and a detector voltage of 2 kV. Mass spectra were recorded between 10 and 600 u with a scan speed of 0.9 s. The precursor was dissolved in chloroform and 1 µl aliquots were injected onto the heated injector with a 30 : 1 split where pyrolysis occurred. Mass spectra of the volatile pyrolyzates were recorded as described above.

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