Decomposition of Allylselenium Sources in the Metalorganic Chemical Vapor Deposition of ZnSe

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Received September 10, 1992. Revised Manuscript Received December 21, 1992

The gas-phase decomposition of methylallyl selenide (MASe) and diallyl selenide (DASe) was studied in a molecular beam mass spectrometric system under conditions used for the metalorganic chemical vapor deposition of zinc selenide (ZnSe). Consistent with reported growth results, the decomposition temperature of DASe was determined to be about 60 °C lower than that of MASe. Pyrolysis experiments carried out in H_2 and He carrier gases showed that allyl selenides decompose by a combination of homolysis and an intramolecular rearrangement pathway, with 1,5-hexadiene and propene being the major hydrocarbon products. By comparison, methylallyl telluride (MATe) was found to decompose almost exclusively by homolysis. Selenoaldehyde products generated by the rearrangement mechanism are concluded to be the source of carbon incorporation into ZnSe films grown using allyl Se sources.

Introduction

Metalorganic chemical vapor deposition (MOCVD) continues to play an important role in the growth of high quality ZnSe and other II–VI semiconductor materials for optoelectronic device applications. Zinc alkyls, such as dimethylzinc (DMZn), have been used in combination with H_2Se to deposit ZnSe films at temperatures around 300–350 °C.[1] The epilayers are of high crystalline quality and have very good electrical and optical properties. However, the films exhibit poor surface morphology and uniformity, which are believed to result from parasitic prereactions between H_2Se and DMZn.[2,3] This behavior, in conjunction with the extreme toxicity of H_2Se, has motivated the investigation of less-reactive Se compounds as alternative sources. Alkyl selenides, such as dimethyl selenide (DMSe) and diethyl selenide (DESe), have been used with DMZn to grow ZnSe layers, at temperatures around 450–500 °C, with good surface morphology, as well as photoluminescence characteristics.[4,5] However, lowering the deposition temperature is of particular interest in the MOCVD of ZnSe in order to reduce native defect formation and also to improve dopant incorporation.[6]

Allyl-based Se compounds, such as methylallyl selenide (MASe) and diallyl selenide (DASe), are thermally less stable than the alkyl selenides and have been used to reduce ZnSe growth temperatures to about 400–450 °C.[7,8] However, ZnSe films grown from allyl Se sources, MASe and DASe, have shown significantly higher levels of carbon incorporation than films grown from the alkyl Se sources.[7] By comparison, allyl Te sources, such as DATe[9] and MATe,[10] have been used to deposit II–VI materials, such as HgCdTe and ZnTe, without any reported problems of carbon incorporation. These differences in the growth results need to be studied in terms of the reaction chemistry of the various source compounds.

Gas-phase decomposition studies of allyl compounds of group VI elements have been reported for sulfur[11] and oxygen.[12] The results suggest that pyrolysis of allyl sulfides and ethers occurs by a rearrangement mechanism which involves a H atom shift in a six-centered ring transition state. The primary products are propene and the corresponding aldehydes (R=O) for ethers and thioaldehydes (R=S) for sulfides, respectively, with R being the organic ligand. On the basis of HgTe growth studies comparing various organotellurium sources, Hoke et al.[13] conclude that homolysis of the C–Te bond is the rate-determining step in the decomposition of the allyl Te sources. A comprehensive GC/MS study[14] of the pyrolysis of organotellurium sources showed that substituted hexadienes were the predominant decomposition product from allyl

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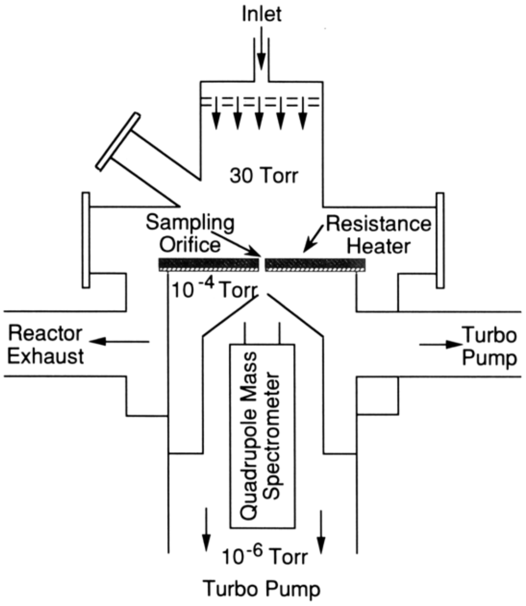

Figure 1. Schematic of stagnation flow MOCVD reactor with molecular beam sampling to a Balzer QMS 311 mass spectrometer.

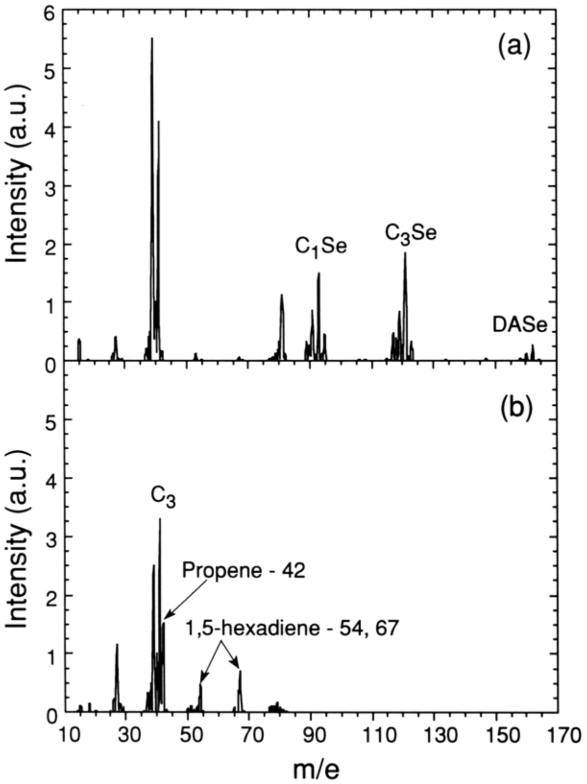

Figure 2. Mass spectra for pyrolysis of DASe in H_2 carrier gas at (a) room temperature (T = 32 °C) and at (b) complete decomposition (T = 470 °C).

Te compounds and suggested that decomposition occurred primarily by bond homolysis. The C–Se bond strength lies between that of C–Te and C–S[15] and the pyrolysis of allyl Se compounds might be expected to occur by a combination of the rearrangement and homolysis pathways. Molecular beam mass spectroscopy data are presented for the gas phase decomposition of the allyl Se and allyl Te compounds to establish the differences in the chemistry affecting the properties of the grown films.

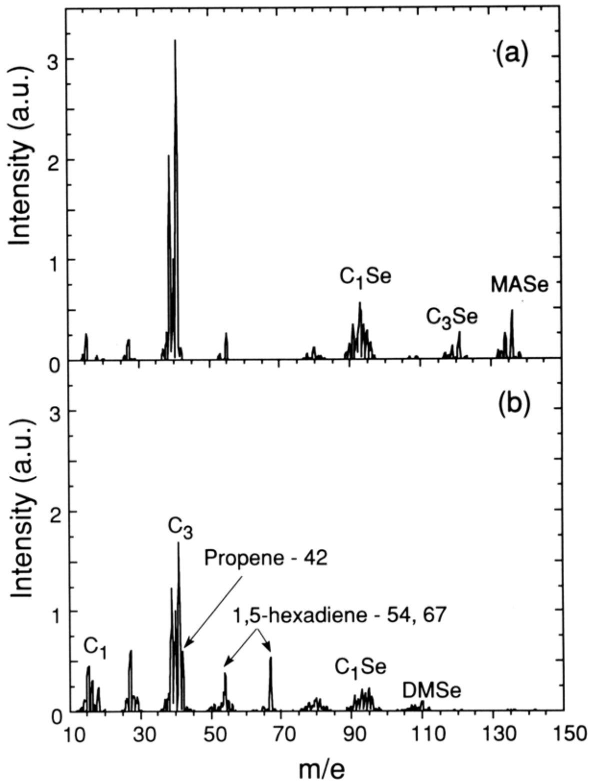

Figure 3. Mass spectra for pyrolysis of MASe in H_2 carrier gas at (a) room temperature (T = 33 °C) and at (b) complete decomposition (T = 475 °C).

Experimental Section

A special vertical, stagnation flow reactor with molecular beam sampling through the susceptor was used to investigate the decomposition of MASe (American Cyanamid) and DASe (Advanced Technology Materials). For comparison, the pyrolysis of an alkyl selenide, DESe (Morton Thiokol), and an allyl telluride, MATe (Advanced Technology Materials), were also studied in the same reactor. The reactor system is shown schematically in Figure 1 and has been described in detail elsewhere.[16] The gas in the reactor was sampled through a 100-μm pinhole in a stainless steel foil in the center of a resistively heated graphite susceptor. The sampled gas stream was expanded into a molecular beam through two differentially pumped stages and collimated by a skimmer toward a Balzers 311 quadropole mass spectrometer. This arrangement emulates the conditions in the growth reactor and enables the in situ analysis of gas-phase species present in the reactor with minimal downstream gas-phase and wall interactions.

The thermal decomposition of the various organometallic Se sources was studied by monitoring peak intensities of parent compounds and reaction products as a function of susceptor temperature. Peak intensities were corrected for thermal expansion of the sampled gas by using a reference peak based on Ar^+. The pyrolysis studies were conducted with H_2 or He as the carrier gas. The reactor was typically maintained at a pressure of 30 Torr with a carrier gas flow rate of 20 sccm. The delivery rate of the organometallic sources, controlled by mass flow controllers, was about 20 μmol/min. The mass spectra were recorded on a personal computer interfaced to the spectrometer system.

Results and Discussion

Typical mass spectra for DASe and MASe in H_2 carrier gas are shown in Figures 2 and 3, respectively. The spectra are presented for two different temperatures: T = 32 °C, where the decomposition is negligible, and T = 470 °C,

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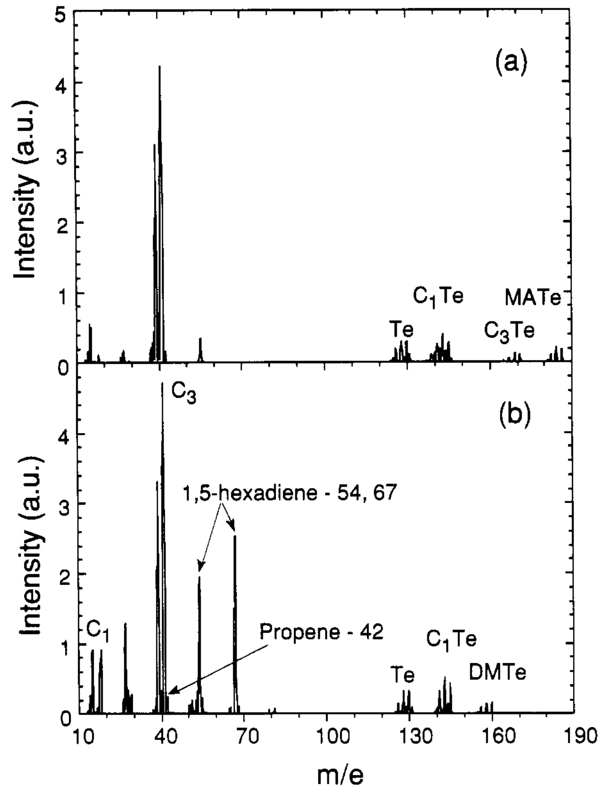


Figure 4. Mass spectra for pyrolysis of MATe in H_2 carrier gas at (a) room temperature (T = 43 °C) and at (b) complete decomposition (T = 366 °C).

where the decomposition of both sources is nearly complete. For comparison, mass spectra of the decomposition products of MATe are also shown in Figure 4, for room temperature, and for T = 370 °C, where this source is completely pyrolyzed. The concentration of the unreacted parent species was followed as a function of temperature by monitoring the intensity of peaks at m/e = 162 for DASe and at m/e = 136 for MASe. The results are plotted in Figure 5a and show that measured at 50% conversion, the decomposition temperature of DASe is about 60 °C lower than that of MASe. Similar decomposition curves for DESe (m/e = 138) and MATe (m/e = 186) have also been shown for comparison in Figure 5b. The pyrolysis temperature data are consistent with the growth results of Patnaik et al.[7] that deposition temperature for ZnSe are reduced by over 100 °C by using DASe as the Se source instead of DESe. The significantly lower decomposition temperature of MATe, as compared to MASe, is indicative of the difference in primary pyrolysis pathways stemming from the weaker carbon–metal bond in MATe than in MASe.

The activation energies for the pyrolysis of MASe and DASe in H_2 carrier gas have been calculated, from the results in Figure 5, based on the assumption of a well-mixed reactor. These values are listed in Table I and are compared to the activation energy for pyrolysis of other allyl chalcogenides. The observed trends of decreasing activation energy are consistent with the weakening carbon–metal bond in going down the group VI elements from oxygen to tellurium.

The various decomposition products were identified by monitoring peak intensities as a function of temperature, after subtracting the contribution from the cracking pattern of the unreacted parent species at each temperature. The normalized intensities of the peaks at m/e = 54 and m/e = 67 are shown at different temperatures in Figure 6 for the pyrolysis of DASe in H_2. The identical trends observed for the intensity of both peaks suggest that they correspond to the cracking pattern of a higher hydrocarbon product. After the onset of decomposition around 225 °C, the ratio of the peak intensities, plotted in Figure 7, remains constant at a value of about 1.5. On the basis of published standard mass spectrometric cracking patterns, the hydrocarbon product was identified as 1,5-hexadiene, which is produced by the combination of allyl radicals generated through homolysis of the parent molecule.

The peak at m/e = 42 corresponds to propene and is present in the mass spectra of the decomposition products of DASe (Figure 2B), as well as MASe (Figure 3b). The decomposition of the sources was carried out in He to determine if the propene is produced by H atom abstraction from the carrier gas by allyl radicals generated during homolysis of the parent species. The decomposition curves for the pyrolysis of DASe in H_2 and in He, plotted in Figure 8, show that the pyrolysis chemistry is not altered by changing the carrier gas. The similar product distribution for the pyrolysis of DASe in H_2 and in He, shown in Figure 9, indicates that the generation of propene is not affected

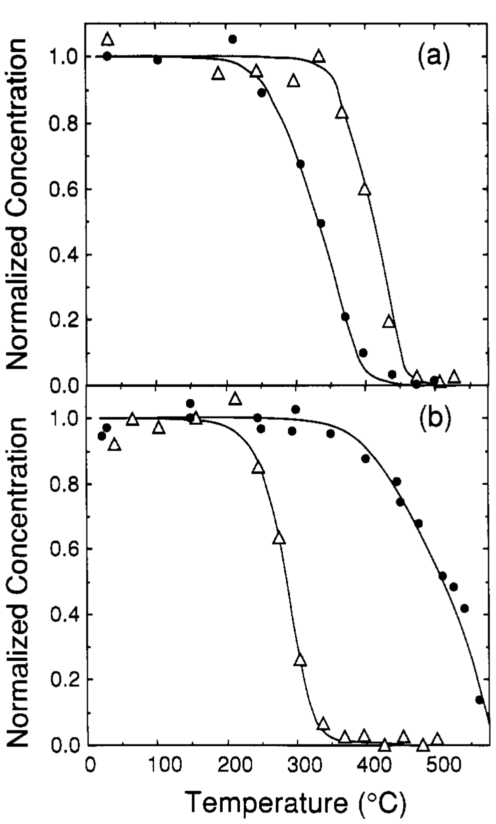


Figure 5. Concentration of unreacted organometallic source, as a function of temperature, in H_2 carrier gas. Concentrations have been normalized with the respective values at room temperature. (a) Decomposition curves for MASe (△) and DASe (●); (b) decomposition curves for MATe (△) and DESe (●).

Table I. Activation Energies for Pyrolysis of Allyl Chalcogenides

chalcogen	activation energy (kJ/mol) methylallyl	 diallyl
oxygen	174.1[12]	171.1[12]
sulfur	159.7[11]	138.2[11]
selenium	159.9	130.9
tellurium	114.8	79.5[9]

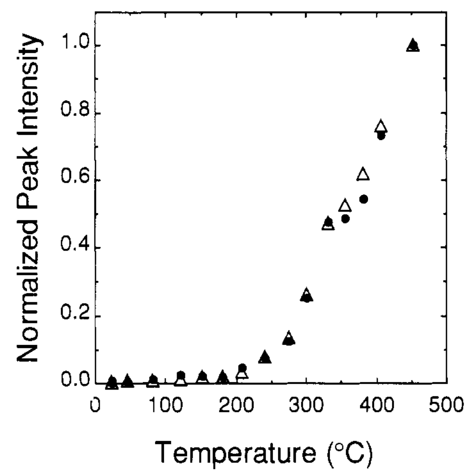


Figure 6. Intensity of peaks at m/e = 54 (▲) and at m/e = 67 (●) as a function of temperature for decomposition of DASe in H_2 carrier gas. Peak intensities have been normalized with the respective maxima.

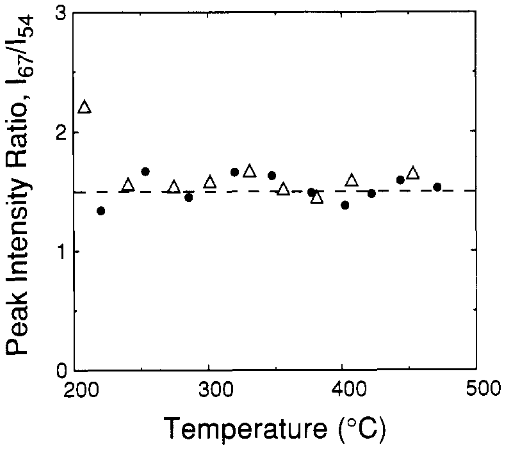
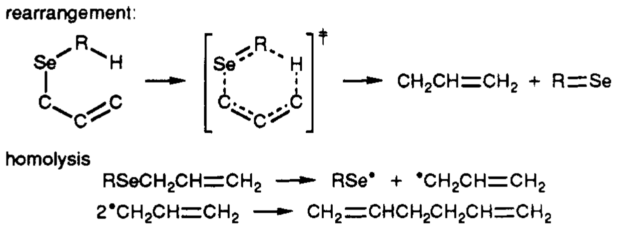


Figure 7. Ratio of peak intensities at m/e = 67 and at m/e = 54 for decomposition of DASe in H_2 (▲) and He (●) carrier gases.

by the carrier gas. The abstraction of H atoms from the organometallic source by the allyl radicals to generate propene is also not expected to be significant at the temperatures of interest.[17] Therefore, the pyrolysis of the allyl Se compounds through the alternative pathway, involving intramolecular rearrangement, is the source of propene detected in the decompsotion products.

On the basis of previous studies on the decomposition of allyl ethers,[12] allyl sulfides,[11] and allyl tellurides,[14] and the mass spectroscopy results presented here, two competing mechanisms may be proposed for the decomposition of allyl selenides:



The relative intensities of the peaks at m/e = 67, corresponding to 1,5-hexadiene, and at m/e = 42, corresponding to propene, is a measure of the competition between the homolysis and rearrangement pathways for decomposition of the allyl compounds. The intensities of these two peaks, normalized to the maximum intensity of the peak at m/e = 67, have been plotted as a function of temperature in Figure 10 for the decomposition of the various allyl compounds in H_2. For DASe (Figure 10a) and MASe (Figure 10b), both propene and 1,5-hexadiene appear simultaneously as the decomposition of the parent compound commences. The relative intensity of the m/e = 42 (propene) peak is greater for DASe as compared to MASe, indicating that the rearrangement pathway, involving a H atom shift between the two organic ligands through the six-centered ring transition state, is more facile in DASe. The decomposition of MATe generates mostly 1,5-hexadiene (Figure 10c), with small amounts of propene appearing only at much higher temperatures. Therefore, in corroboration with the results of Kirss et al.,[14] homolysis was found to be the primary pathway for the decomposition of MATe. On the other hand, the pyrolysis of DASe and MASe results in the generation of both propene and 1,5-hexadiene, suggesting a balance between the rearrangement and homolysis decomposition pathways. These observations are also consistent with the reported results on the pyrolysis of allyl sulfides[11] and ethers,[12] which is believed to occur exclusively by rearrangement.

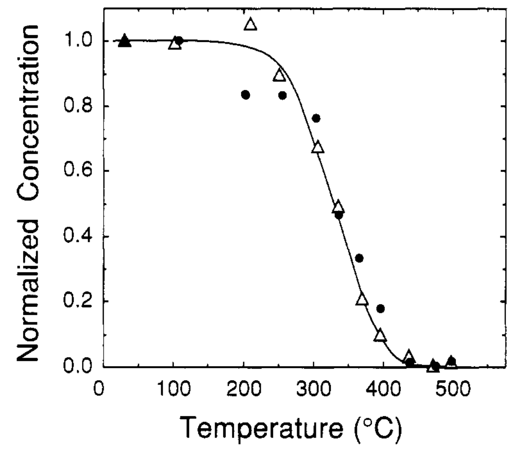


Figure 8. Effect of carrier gas on decomposition curves for DASe: H_2 (▲) and He (●).

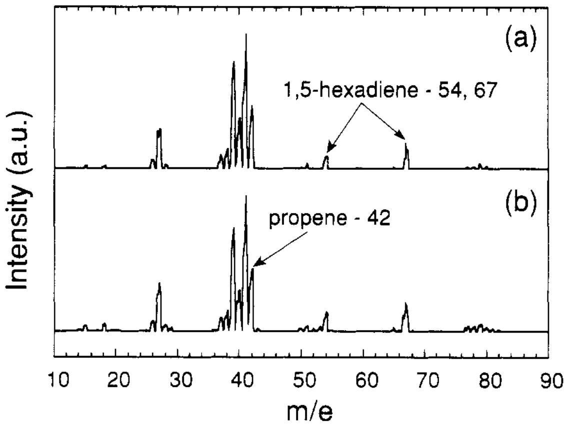


Figure 9. Effect of carrier gas on product distribution for DASe pyrolysis at T = 471 °C; (a) He carrier gas and (b) H_2 carrier gas.

The peaks in the mass spectra corresponding to Se-bearing species were also monitored as a function of temperature to identify the non-hydrocarbon products of decomposition. For DASe, the intensity of the mass spectrometer peaks for all Se-containing species decreases

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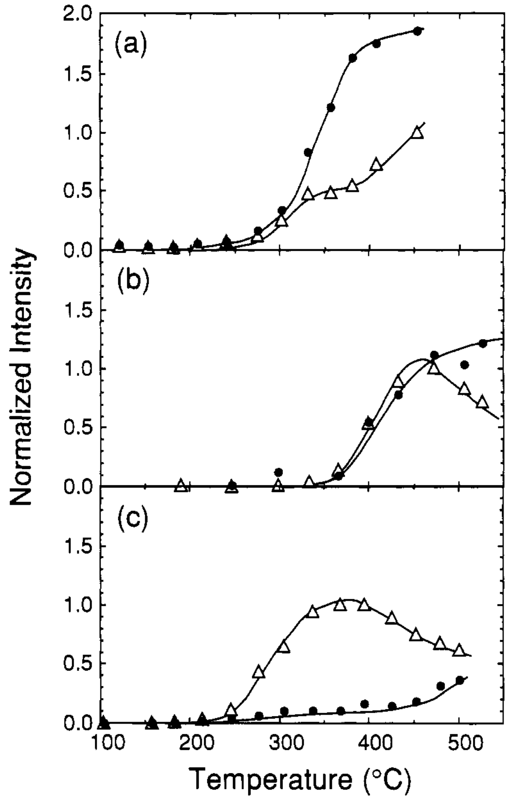

Figure 10. Intensity of peaks at $m/e = 67$ (△) and at $m/e = 42$ (●) as a function of temperature for pyrolysis of (a) DASe, (b) MASe and (c) MATe in H_2 carrier gas. Peak intensities have been normalized with the maximum intensity of the peak at $m/e = 67$.

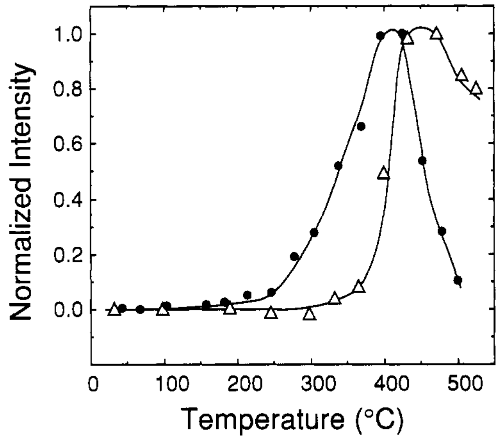

Figure 11. Formation of (△) DMSe during MASe pyrolysis and (●) DMTe during MATe pyrolysis in H_2 carrier gas. Peak intensities have been normalized with the respective maxima.

with increasing temperature, following the same trend as the parent species ($m/e = 162$). On the other hand, during the pyrolysis of MASe, the appearance of peaks at $m/e = 110$, as shown in Figure 11, corresponds to the formation of dimethyl selenide (DMSe). Similarly, the formation of dimethyl telluride (DMTe) ($m/e = 160$) was observed in the pyrolysis of MATe and has also been reported in previous studies.[18] At higher temperatures, both the DMSe and DMTe start to decompose, as well, and result in the generation of methane.

The Se-bearing products of the pyrolysis, R=Se from rearrangement, and RSe• from homolysis, were not observed in the mass spectrometer. In pyrolysis studies of allyl sulfides, Martin et al.[11] found polymeric thioaldehydes to be the primary sulfur-containing reaction product. The selenoaldehydes (R=Se) are expected to be unstable and would tend to oligomerize in a similar manner, and to deposit out on the reactor walls. The RSe• radicals can be expected to recombine to produce diselenides that may, in turn, decompose to produce more stable monoselenides. Dimethyl selenide (DMSe), detected during the pyrolysis of MASe, likely forms by the recombination of $CH_3Se^\bullet$ radicals as

$$2CH_3Se^\bullet \rightarrow CH_3SeSeCH_3$$

$$CH_3SeSeCH_3 \rightarrow CH_3SeCH_3 + Se$$

While the equivalent ditelluride product has been observed by Kirss et al.[14] in a GC/MS study of the pyrolysis of MATe, only the more stable monochalcogenides were detected in our experimental system. The long contact times, resulting from the well-mixed reactor configuration used in this experimental setup, cause the decomposition of the unstable dialkyl dichalcogenides into the more stable dialkyl selenides and tellurides.

Since allyl tellurides decompose almost exclusively by homolysis, RTe• radicals are the Te bearing precursors leading to film growth. HgTe films grown from MATe[10] and DATe[9] were not reported to show any significant levels of carbon incorporation, indicating that the organic ligand is easily volatilized from the RTe• precursor on incorporation into the growing film. RSe• radicals and selenols (RSeH) produced by homolysis and β-hydrogen elimination, respectively, in alkyl Se sources such as DESe,[19] also do not result in the incorporation of carbon into the growing film, except at very high VI/II ratios.[8] However, characterization by SIMS of ZnSe films grown from allyl Se sources, shows significant levels of carbon incorporation.[7] The selenoaldehyde (R=Se) product of rearrangement, and the RSe• radicals produced by homolysis, are the Se-bearing precursors in growth from allyl Se sources. On incorporation at the growth interface, the selenoaldehyde is less likely to lose its organic ligand and is the likely source of carbon in the ZnSe films grown from allyl selenides. The larger ratio of mass 42 to mass 67 observed for DASe than for MASe indicates that the rearrangement reactions occur more for DASe than MASe and one would then have expected to see a larger degree of carbon incorporation with the diallyl reagent. However, growth results show less carbon incorporation with DASe than MASe. This effect may be attributed to the surface reactions of the selenoaldehydes. $CH_2{=}CHCH{=}Se$ polymerizes less readily than $CH_2{=}Se$, and the larger aldehyde has more pathways for forming a stable, volatile hydrocarbon product. Therefore, although more of the DASe undergoes the intermolecular rearrangement, the product does not incorporate carbon into the films as effectively as $CH_2{=}Se$.

Conclusion

The potential of reduced temperature MOCVD of ZnSe using allyl Se sources, such as MASe and DASe, is offset by the high levels of carbon observed in the grown films. By comparison with the pyrolysis of other allyl chalco-

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genides, the mass spectroscopic identification of the decomposition products of the pyrolysis of allyl selenides reveals a balance between homolysis and rearrangement pathways for decomposition. The Se-bearing growth precursor generated by the rearrangement pathway is a selenoaldehyde (R=Se), which is the likely source of carbon incorporation into the growing film. Unsymmetric allyl selenides, which are designed to block the rearrangement pathway for decomposition while taking advantage of the lower thermal stability stemming from the allyl group, may still realize the potential of MOCVD of high quality ZnSe from organometallic Se sources.

Acknowledgment. This work was supported by the National Science Foundation and the Strategic Defense Initiative Organization.