Gas-Phase Pyrolysis of *tert*-Butyl(allyl)selenium, a New Precursor for Organometallic Chemical Vapor Deposition of ZnSe

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The gas-phase pyrolysis mechanism of *tert*-butyl(allyl)selenium (tBASe), a new organometallic chemical vapor deposition (OMCVD) precursor for ZnSe, was probed under reduced pressure flow conditions by molecular beam mass spectrometry (MBMS). The precursor decomposed in a hydrogen carrier gas above 180 °C to selenium, propene, 2-methylpropene, 2-methylpropane, 1,5-hexadiene, diallylselenium (DASe), and hydrogen selenide. Pyrolysis in deuterium did not result in any isotope exchange between the carrier gas and pyrolysis products. A mechanism involving β-hydrogen transfer and homolysis of the Se–C bonds as the primary decomposition pathways is proposed. Copyrolysis of tBASe with dimethylzinc (DMZn) in hydrogen yielded methane, propene, 2-methylpropene, 1,5-hexadiene, methyl-(allyl)selenium (MASe), and dimethylselenium (DMSe) as the major volatile products. The underlying mechanism for formation of selenium byproducts is described, and the impact of the pyrolysis chemistry on growth and carbon incorporation is discussed.

Introduction

Epitaxial films of ZnSe and related alloys are important materials for short-wavelength optoelectronic devices, *e.g.*, green-blue light-emitting diodes and diode lasers.[1,2] High optoelectronic quality ZnSe films can be grown on GaAs substrates by organometallic chemical vapor deposition (OMCVD) from hydrogen selenide and dimethylzinc (DMZn) or its triethylamine adduct (DMZn-NEt₃).[3] However, a parasitic gas-phase reaction between the precursors leads to a poor surface morphology and thickness uniformity. In addition, the extreme toxicity of H₂Se (LD = 50 ppb), in combination with its high vapor pressure (approximately 9100 Torr at 31 °C), raises serious safety problems. Hence, a variety of dialkylselenium compounds has been tested in the OMCVD process to replace H₂Se.[4] Although low molecular weight selenium dialkyls, such as dimethylselenium (DMSe) and diethylselenium, allow deposition of films with improved morphology, relatively high

growth temperatures, typically above 450–500 °C, are necessary to achieve acceptable growth rates.[5] Such high temperatures are detrimental to the quality of the ZnSe films. Therefore, particular attention has been paid to synthesis of organoselenium precursors which would facilitate low temperature OMCVD of epitaxial ZnSe.

Dialkylselenium compounds with allyl and *tert*-butyl substituents, groups yielding electronically stabilized free radicals upon decomposition, are promising reagents for the low temperature growth. Methyl(allyl)-selenium (MASe) and diallylselenium (DASe) were used for growth of epitaxial ZnSe at 400–450 °C.[6] Unfortunately, the films were heavily contaminated with carbon exceeding concentration levels of 10²⁰–10²¹ atoms/cm³. A gas-phase pyrolysis study under OMCVD growth conditions pointed to selenoaldehyde intermediates formed by the retro-ene reaction of the allylselenium compounds as the source of the carbon incorporation.[7] Kuhn et al. used di-*tert*-butylselenium (DtBSe) for low-temperature growth of epitaxial ZnSe under atmospheric pressure OMCVD conditions.[8] The films showed excellent crystallinity and sharp near-band-edge photoluminescence. Taudt et al. recently attempted to

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employ DtBSe for OMCVD growth of nitrogen-doped ZnSe.[9]

tert-Butyl(allyl)selenium (tBASe) is a new selenium precursor designed to facilitate low temperature OM-CVD of epitaxial ZnSe.[10] In contrast to MASe and DASe, the retro-ene decomposition channel is not accessible for tBASe because of the presence of the *tert*-butyl group, and low carbon contamination of the films would then be expected. This expectation was verified in OMCVD experiments in which layers of low carbon concentration levels, below the detection limit of secondary ion mass spectroscopy (SIMS $\sim 5 \times 10^{17}$ atoms/cm^3), were prepared from tBASe and DMZnNEt$_3$.[10] The grown layers showed excellent crystallinity and a sharp excitonic photoemission. Even though these results are consistent with the proposed pyrolysis pathways,[10] specifically β-hydrogen transfer and homolysis of the Se–C bonds, alkyl redistribution reactions in the presence of the zinc precursor might result in deterioration of the material quality at certain growth conditions. In addition, the redistribution reactions may also limit the conversion of tBASe into ZnSe since thermally stable byproducts, such as DMSe, would not contribute to the deposition at low temperatures. Therefore, gas-phase pyrolysis of tBASe was probed under OMCVD conditions to gain insight into the OMCVD chemistry of the precursor and to assess the critical growth parameters for preparation of high quality ZnSe films. The results of the gas-phase pyrolysis study are correlated with data from our previous OMCVD experiments with tBASe, MASe, and DASe, specifically with the carbon content in the ZnSe layers as determined with SIMS.[6,10]

Experimental Section

General Procedures. Synthesis and reagent manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques, vacuum lines, and a Vacuum Atmospheres glovebox. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded at room temperature in benzene-d_6 on a WP 200SY NMR spectrometer equipped with a VSP200 broad band probe. ^{77}Se spectra were proton decoupled and referenced to Ph$_2$Se at 402 ppm. ^{1}H and ^{13}C spectra were referenced to solvent peaks. The vapor pressure of tBASe was measured in a high-vacuum system equipped with a MKS Baratron in the range 19–45 °C.

tert-**Butyl(allyl)selenium.** To a solution of diallylselenium (Advanced Technology Materials, Inc., 50.3 g, 0.312 mol) in THF (450 mL) cooled to −77 °C was added *tert*-butyllithium (1.6 M in pentane, 0.376 mol) over 30 min. The reaction mixture was allowed to stir for 1 h at −77 °C and then quenched by cautious additions of degassed water. After warming to room temperature, the solution was filtered through silica and solvent was removed by distillation at atmospheric pressure. Vacuum distillation of the product at 60–62 °C and 10 Torr gave a colorless liquid; yield 36 g, 0.203 mol, 65%. NMR (C$_6$D$_6$) ^{1}H δ (ppm) 1.30 (s, 9H), 3.09 (d, 2H, 7 Hz), 4.83 (d, 1H, 10 Hz), 4.98 (d, 1H, 17 Hz), 5.90 (m, 1H); ^{13}C δ (ppm) 25.0, 32.8, 115.9, 136.7; ^{77}Se δ (ppm) 359. Vapor pressure: log (P[Torr]) = 7.846 − 2164/T[K].

Gas-phase pyrolysis was carried out at 30 Torr under steady state flow conditions in a custom-made molecular beam mass spectrometric system (MBMS) described in more detail elsewhere.[11] The MBMS system emulates the flow characteristics of the stagnation point OMCVD reactor used for the growth

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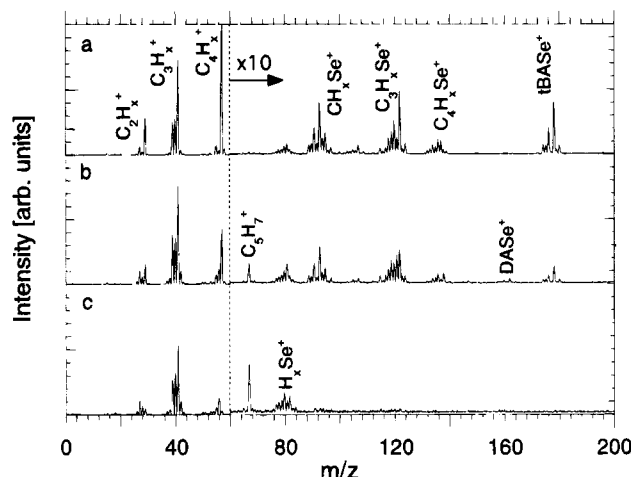

Figure 1. Molecular beam mass spectra of the gas phase recorded during pyrolysis of tBASe in hydrogen at 100 (a), 240 (b), and 440 °C (c). The spectra are corrected for the temperature dependence of the sampling flux.

experiments with tBASe and the other allylselenium precursors.[6,10] In the MBMS system, the gas phase from the vicinity of a resistively heated graphite susceptor was sampled through a 100 μm pinhole into a high-vacuum expansion chamber and collimated with a skimmer into a differentially pumped chamber toward a Baltzers 311 quadrupole mass analyzer. The molecular beam sampling allowed monitoring the composition of the gas phase without interfering with post-sampling reactions.

The delivery rates of the organometallics were maintained at 20 μmol/min using a hydrogen (UHP, Matheson) or deuterium (99.9%, Matheson) carrier gas with a total flow rate of 25 standard cm^3/min (sccm). Prior to the pyrolysis experiments the inner surfaces of the reactor were exposed to the organometallics at heater temperature $\sim$500 °C. The molecular beam mass spectra were recorded at various susceptor temperatures and corrected for the temperature dependence of the sampling flux. The partial pressures of the gas-phase species were determined from the MBMS intensities at the characteristic m/z values: methane, 16, ethane, 30, propene, 42, 2-methylpropane, 43, 2-methylpropene, 56, 1,5-hexadiene, 67, DMZn, 64 and tBASe, 178. The spectrometer sensitivity factors were obtained in separate calibration experiments with the individual compounds. The contribution of the fragmentation pattern of tBASe and DMZn to the characteristic signals of the decomposition products was subtracted from the partial pressure data.

Results and Discussion

MBMS Pyrolysis of tBASe in Hydrogen. Mass spectra of tBASe obtained during gas-phase pyrolysis in a hydrogen carrier gas are shown in Figure 1 for three susceptor temperatures. The spectrum at 100 °C corresponds to tBASe without any decomposition products (Figure 1a). At this temperature, there is also no indication of alkyl redistribution reactions resulting in formation of DtBSe and DASe. At 240 °C, the precursor is partially pyrolyzed and the gas-phase contains propene, 2-methylpropene, 2-methylpropane, 1,5-hexadiene, and hydrogen selenide (Figure 1b). In addition, a weak signal of DASe, a byproduct of the pyrolysis, can be detected at this intermediate temperature. At 440 °C, tBASe is completely decomposed and the spectrum shows hydrocarbon products, hydrogen selenide, and elemental selenium (Figure 1c). The decay of tBASe

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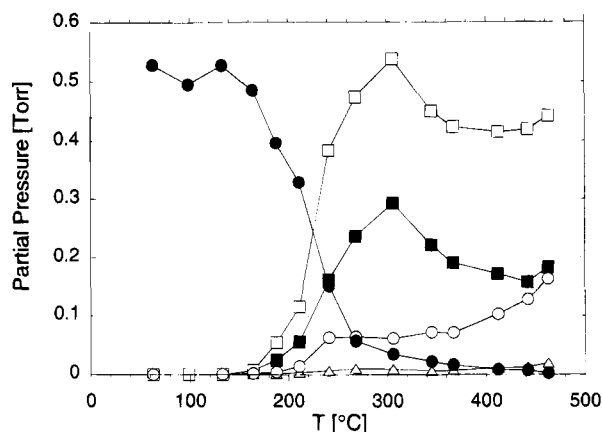*Chem. Mater., Vol. 7, No. 4, 1995* **733**

Figure 2. Partial pressures of tBASe and the hydrocarbon products in the gas phase during pyrolysis of tBASe in hydrogen at various temperatures; (●) tBASe, (■) propene , (□) 2-methylpropene, (△) 2-methylpropane, and (○) 1,5-hexadiene.

Figure 3. Partial pressure ratios of propene vs 1,5-hexadiene (●) and 2-methylpropene vs 2-methylpropane (□) for the pyrolysis of tBASe in hydrogen.

and the evolution of the hydrocarbon products are shown in Figure 2 as a function of the pyrolysis temperature. The precursor starts to decompose in a hydrogen carrier gas above ~180 °C and the pyrolysis is complete by ~340 °C. The apparent activation energy for the pyrolysis process, calculated using a well-stirred reactor model, is ~25 kcal/mol. This value nearly equals the apparent activation energy for OMCVD growth, even though the temperature required for complete conversion of tBASe is low compared to the transition temperature of ~400 °C between kinetically controlled and transport limited growth, i.e., very fast deposition.[10,12]

Propene, 2-methylpropene and 1,5-hexadiene are the major hydrocarbon pyrolysis products (Figure 2). The partial pressures of propene and 2-methylpropene increase sharply with the onset of the tBASe decomposition and reach a maximum at ~300 °C. The ratios of propene vs 1,5-hexadiene partial pressures and 2-methylpropene vs 2-methylpropane partial pressures are shown in Figure 3 for various pyrolysis temperatures. Propene and 1,5-hexadiene originate from the allyl group of tBASe, while 2-methylpropene and 2-methylpropane are formed from the *tert*-butyl group of the precursor. The ratios of these hydrocarbons indicate that formation of 1,5-hexadiene and 2-methylpropane becomes more favorable at increasing pyrolysis temperature. The latter hydrocarbon remains, however, a minor product even at ~450 °C. The signal of DASe can be detected in the range 180–350 °C with a peak intensity at 240 °C (Figure 4). The decay of the signal of DASe above ~250 °C is consistent with thermal decomposition of DASe.[7] The conversion of tBASe to DASe was approximately 10% as estimated from the relative intensities of the parent signals. A reliable quantification of the hydrogen selenide and selenium MBMS signals is difficult since both species are present in the fragmentation patterns of tBASe and DASe. However, these species can be clearly identified at high
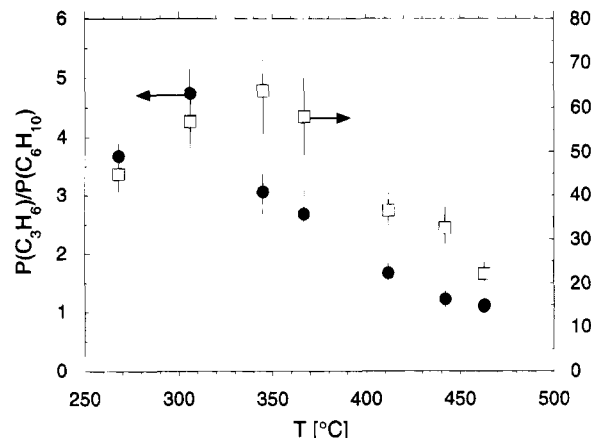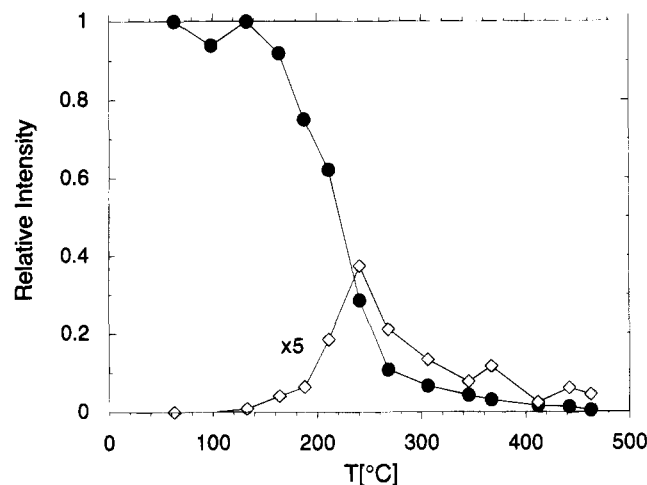

Figure 4. Relative MBMS intensities of tBASe and DASe from the pyrolysis of tBASe in hydrogen. (●) tBASe (m/z = 178 amu) and (◇) DASe (m/z = 162 amu).

temperatures when the selenium dialkyls are completely decomposed. The MBMS spectra did not show any evidence of formation of DtBSe.

The role of the carrier gas in the OMCVD of II–VI semiconductors is often a subject of controversy. We probed the effect of a hydrogen carrier gas on the decomposition mechanism of tBASe by conducting the pyrolysis in deuterium. Theoretically, any mechanism activating the carrier gas, either in the gas-phase or on the surfaces of the reactor, should result in formation of deuterated hydrocarbons and increase of the HD partial pressure. Figure 5 shows the hydrocarbon region of the mass spectra acquired in deuterium and hydrogen carrier gases at three pyrolysis temperatures. We observed only a slightly lower decomposition temperature in comparison with the pyrolysis in hydrogen, presumably caused by a lower purity of the deuterium gas (99.9%). However, the spectra show no evidence of deuterated hydrocarbons at pyrolysis temperatures up to 450 °C. Consistently, no indication of isotope exchange in the HD region was observed (not shown).

The pyrolysis of tBASe can be described with a mechanism involving homolytic scission of the Se–C bonds and β-hydrogen elimination as the primary decomposition steps (Scheme 1). The *tert*-butyl group facilitates both homolysis of the Se–C bond (path **a**) and β-hydrogen elimination (path **b**). The low decomposition

(12) This discrepancy in growth and pyrolysis behavior is most likely caused by the difference in residence times between pyrolysis experiments and OMCVD growth. The residence time in the MBMS system was ~300 s, while the residence time in the OMCVD reactor was ~10 s. The longer exposure of the precursor in the hot zone of the MBMS system results in a higher conversion of the precursor than in the OMCVD reactor.
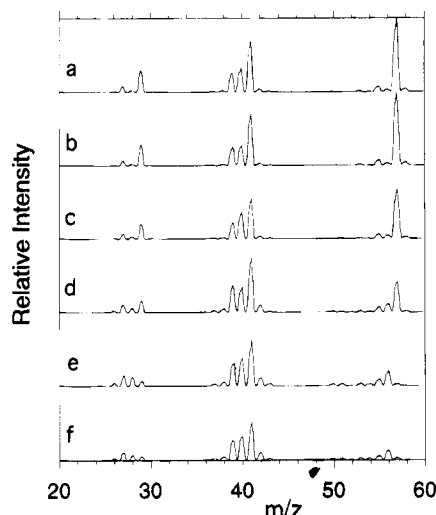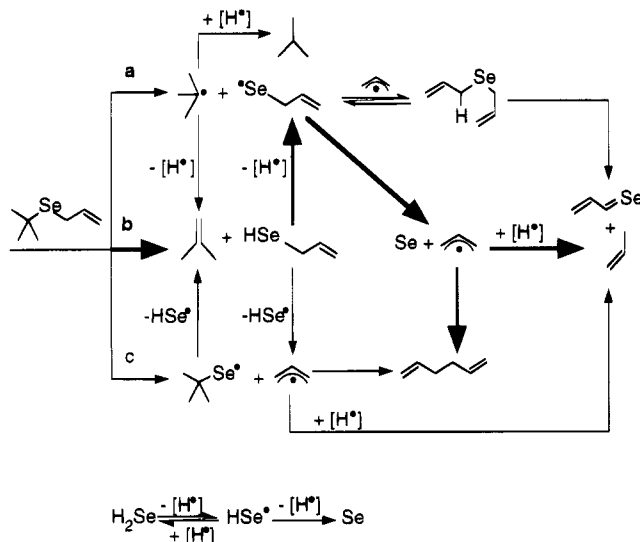
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Figure 5. Hydrocarbon region of molecular beam mass spectra recorded during pyrolysis of tBASe in deuterium and hydrogen: (a) 100 °C in deuterium, (b) 100 °C in hydrogen, (c) 250 °C in deuterium, (d) 240 °C in hydrogen, (e) at 450 °C in deuterium, and (f) 440 °C in hydrogen.

Scheme 1. Pyrolysis Mechanism of tBASe under Reduced Pressure OMCVD Conditions[a]

[a] The major low-temperature reactions are shown with bold arrows. The symbol [H•] stands for hydrogen radical donors.

temperature of DtBSe, as verified in OMCVD experiments,[9] suggests that at least one of these pathways should be feasible at 300–350 °C. The third decomposition step, homolysis of the Se–C(allyl) bond, yielding *tert*-butylselenium radical and resonance stabilized allyl radical (path **c**), is characteristic of alkyl(allyl)selenium compounds and is accessible below ~350 °C.[7] The decomposition temperature of tBASe (~230 °C, determined at a 50% conversion) is, however, significantly reduced in comparison to the temperatures for DASe (~330 °C) and MASe (~410 °C) observed in the MBMS under identical experimental conditions.[7] This higher reactivity of tBASe, in comparison to DASe and MASe, is also reflected in the OMCVD characteristics of the allylselenium precursors.[10] For example, the transition to the transport limited growth for tBASe was observed at ~ 400 °C, compared with ~440 °C for DASe and ~470 °C for MASe. Thus, the comparison of the relative thermal stabilities of tBASe, DASe, and MASe under

OMCVD conditions suggests that the low temperature decomposition path of tBASe originates from the reactivity of the *tert*-butyl moiety.

The presence of 2-methylpropene and 2-methylpropane is consistent with gas-phase disproportionation of the *tert*-butyl radicals formed by homolysis of the Se–C(*tert*-butyl) bond (path **a**). If path **a** were the only decomposition reaction, a nearly equimolar 2-methylpropene vs 2-methylpropane ratio could be expected due to the tendency of free *tert*-butyl radicals to disproportionate.[13] However, the observed ratio ranging from 20 to 70 (Figure 3) indicates only a minor contribution of path **a** to the overall conversion of tBASe. In contrast to these large values, a ratio of ~2 was found for gas-phase pyrolysis of *tert*-butyl(allyl)tellurium.[14] For the tellurium compound, path **a** is favored by the lower strength of Te–C bond resulting in increased abundance of 2-methylpropane in the pyrolysis products.

The large ratios of 2-methylpropene vs 2-methylpropane partial pressures (Figure 3) are consistent with a significant contribution of β-hydrogen elimination (path **b**) in the overall decomposition mechanism of tBASe. This is not surprising since β-hydrogen elimination significantly contributes to the overall pyrolysis mechanisms of related *tert*-butylsulfur[15] and *tert*-butyltellurium compounds.[14,16] The intermediate allylselenol is expected to be unstable under the pyrolysis conditions. A direct observation of the intermediate is further complicated by interference with the fragmentation pattern of the other allylselenium species present in the gas phase.

Provided path **b** dominates decomposition of tBASe, understanding the pyrolysis chemistry of allylselenol seems to be essential for a mechanistic insight into the OMCVD chemistry of the precursor. Cole-Hamilton et al. showed that the main gas-phase pyrolysis pathway of aliphatic selenols is scission of the Se–H bond.[17] Reductive elimination of alkane and scission of the Se–C bond were found to be only minor pyrolysis channels. On the basis of these results we assume that the scission of Se–H bond is also the major decomposition path of allylselenol. The allylselenium radical, formed by this reaction, will likely undergo a consecutive scission of the Se–C bond yielding elemental selenium and allyl radicals.[17] Alternatively, the allylselenium radical will recombine with a free allyl radical to form the observed DASe.

Theoretically, 2-methylpropene may also be formed along the radical path **c**. *tert*-Butylselenium radicals could undergo tautomerization involving hydrogen atom transfer from one of the methyl groups to the selenium atom, and subsequent decomposition to a hydrogen selenium radical and 2-methylpropene. Benson has pointed to significance of such a mechanism for pyrolysis

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of *tert*-butylsulfur compounds.[18] However, an identical mechanism seems to be less likely for the pyrolysis of *tert*-butylselenium compounds where the scission of C—H bond and formation of the weak Se—H bond[19] is less favorable on a thermodynamic basis. Alternatively, 2-methylpropene and a hydrogen selenium radical might be formed from the *tert*-butylselenium radical by a concerted reaction involving β-hydrogen transfer. In either case, the rate of the elimination reaction would have to be faster than the competing homolysis of the Se—C(*tert*-butyl) bond since the pyrolysis data argue for a negligible amount of *tert*-butyl radicals being present in the gas phase. Nevertheless, path **c** is likely a minor decomposition channel at temperatures below ~300 °C, and it cannot account for the large quantity of 2-methylpropene observed at the low temperatures. This conclusion is consistent with absence of DtBSe and di-*tert*-butyldiselenium, expected products of recombination reactions of *tert*-butylselenium radicals.

The allyl radicals formed by scission of the Se—C(allyl) bonds may undergo either hydrogen abstraction reactions or radical recombinations. The former reactions account for the formation of propene, while the latter mechanism explains the presence of 1,5-hexadiene. It is important to note that propene is also a product of reductive elimination reaction of allylselenol and retro-ene rearrangement of DASe. However, the contribution of these two mechanisms to the overall formation of propene is marginal due to the low probability of the reductive elimination pathway of selenols[17] and a low conversion of tBASe to DASe. Thus, the major reaction yielding propene is hydrogen abstraction and selenium species containing the weak Se—H bonds, such as allylselenol, are most likely to be the hydrogen donor. The radical recombination, the alternative reaction of free allyl radical, becomes the dominant reaction channel at high temperatures (Figure 3). This temperature effect is consistent with increasing probability of a radical decomposition mechanism, specifically with increasing contribution of path **c**.

Hydrogen selenium radicals formed from allylselenol or from *tert*-butyl selenium radicals will undergo hydrogen abstraction reactions. These reactions could account for the presence of hydrogen selenide, but their contribution to the overall pyrolysis mechanism is probably marginal. The presence of good hydrogen donors in the gas-phase, such as hydrogen selenide and allylselenol, may be detrimental to OMCVD growth of p-type ZnSe. Recent studies showed that incorporation of hydrogen into the layers and formation of N—H complexes resulted in compensation of p-type conductivity.[20]

MBMS Pyrolysis of tBASe and DMZn in Hydrogen. Addition of DMZn into the flux of tBASe does not result in any detectable decay of the intensity of the tBASe parent signal up to ~100 °C. This observation is consistent with a negligible gas-phase prereaction between the precursors after mixing.[10] Mass spectra of pyrolysis of an equimolar mixture of tBASe and

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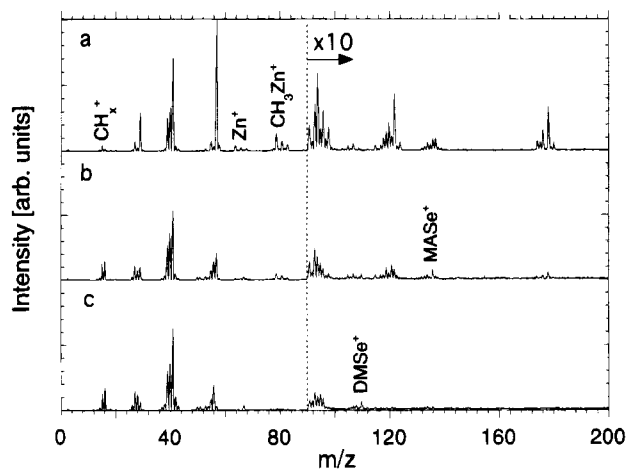

Figure 6. Molecular beam mass spectra of the gas phase from the copyrolysis of an equimolar mixture of tBASe and DMZn in hydrogen at 100 (a), 320 (b), and 450 °C (c). The spectra are corrected for the temperature dependence of the sampling flux.
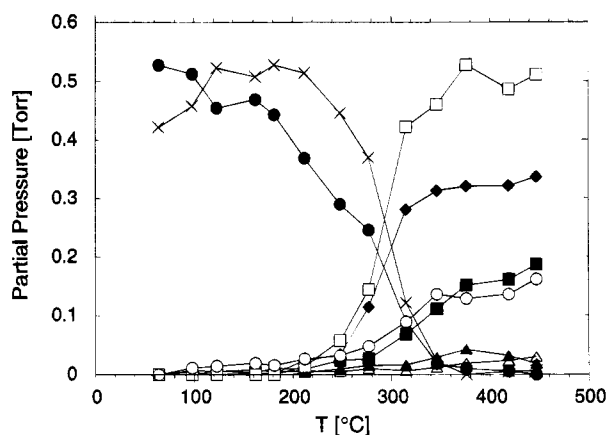

Figure 7. Partial pressures of tBASe, DMZn, and the hydrocarbon products from the copyrolysis of tBASe and DMZn in hydrogen at various temperatures; (●) tBASe, (×) DMZn, (◆) methane , (▲) ethane, (■) propene, (□) 2-methylpropene, (△) 2-methylpropane, and (○) 1,5-hexadiene.

DMZn in a hydrogen carrier gas are shown in Figure 6 for three different temperatures. The spectrum at 100 °C corresponds to superposition of the precursors spectra (Figure 6a). At 317 °C the gas phase contains small quantities of tBASe and DMZn along with methane, propene, 2-methylpropene, and 1,5-hexadiene as the major decomposition products (Figure 6b). Traces of ethane, 2-methylpropane, DMSe, MASe, and DASe can be detected at this temperature. At 450 °C both precursors are pyrolyzed and the gas phase contains the hydrocarbon products with traces of elemental selenium (Figure 6c). The signals of DASe and MASe have almost disappeared, while the signal of DMSe is increased. No indication of DtBSe formation was observed.

Figure 7 displays the partial pressures of tBASe, DMZn, and the hydrocarbon products at various pyrolysis temperatures. The onset of tBASe decomposition remains essentially unaffected by the presence of DMZn. However, the apparent activation energy of the decomposition of tBASe in the presence of DMZn is slightly reduced in comparison to the pyrolysis of tBASe. The decomposition of DMZn follows the decay of tBASe and both precursors are pyrolyzed completely by ~380 °C.

The partial pressures of the hydrocarbon pyrolysis products increase with the conversion of the precursors
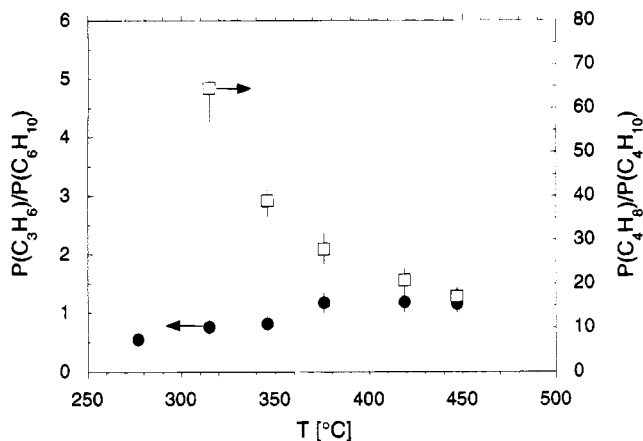
Figure 8. Partial pressure ratios of propene vs 1,5-hexadiene (●) and 2-methylpropene vs 2-methylpropane (□) for the copyrolysis of tBASe and DMZn in hydrogen.

(Figure 7). 2-Methylpropene remains the most abundant hydrocarbon for the pyrolysis of tBASe without the presence of DMZn. The partial pressure data for 2-methylpropene might contain some contribution of 1-butene, the expected product of recombination of methyl radicals from DMZn with allyl radicals. The difficulty in differentiating between 2-methylpropene and 1-butene in the MBMS stems from almost identical fragmentation patterns of the isomers. However, the mass balance of the C_3, C_4, and C_6 hydrocarbons for pyrolysis temperatures above 400 °C indicates that the amount of 1-butene would not exceed ~10% of the overall signal at $m/z = 56$. The gas phase contains only traces of 2-methylpropane and the ratios of 2-methylpropene vs 2-methylpropane decrease with the pyrolysis temperature in a similar manner as for the pyrolysis of tBASe (Figure 8). The presence of DMZn reduces the formation of propene at intermediate temperatures (250–400 °C) in favor of 1,5-hexadiene as compared to the pyrolysis of tBASe (Figure 8). However, at high temperatures (above 400 °C) the ratio of propene vs 1,5-hexadiene converges to the values found for tBASe. The partial pressure of methane increases with the pyrolysis temperature, while the formation of ethane slightly decreases above ~380 °C (Figure 7). The partial pressures of methane and ethane account only for ~50% of the DMZn flux. It is expected that the methyl groups in the fluxes of MASe, DMSe, and 1-butene represent the remaining 50%.

The relative intensities of the parent signals of tBASe, DASe, MASe and DMSe formed during the copyrolysis of tBASe and DMZn are shown in Figure 9. In comparison to the pyrolysis of tBASe (Figure 4), the quantity of DASe is reduced by a factor of ~4. The intensity of the MASe signal starts to increase with the onset of tBASe decomposition, reaching a maximum at ~300 °C. Above this temperature the signal starts to decay due to thermal decomposition of the compound.[7] Conversely, the signal of DMSe keeps increasing with the pyrolysis temperatures. Assuming the same sensitivity factors for the parent signals, the conversion of tBASe into the selenium side products is roughly 30%. Even though the presence of DMZn results in an increase of overall conversion of tBASe into selenium byproducts, the partial pressure of DASe, a species significantly contributing to the carbon level in the layers, is negligible (<3%).
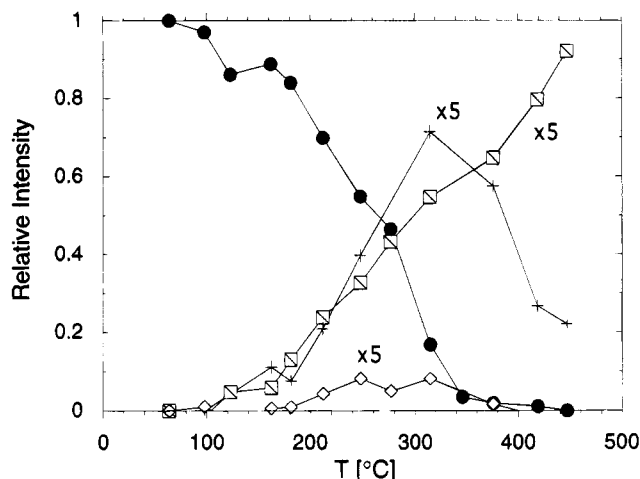

Figure 9. Relative MBMS intensities of tBASe, DASe, MASe, and DMSe from the pyrolysis of tBASe in hydrogen at various temperatures; (●) tBASe ($m/z = 178$ amu), (◇) DASe ($m/z = 162$ amu), (+) MASe ($m/z = 136$), and (□) DMSe ($m/z = 110$ amu).

The mechanism of the copyrolysis of tBASe and DMZn is complex and the MBMS allows only observation of volatile species. Thus, the mechanistic details about the reactions between the precursors resulting in formation of nonvolatile products remain obscured. However, some conclusions relevant for the mechanism of the growth can be derived from the MBMS data. The mass spectra of the tBASe/DMZn mixture showed a negligible gas-phase prereaction between the precursors at room temperature. Such stability of the reagents is important for uniform growth and good surface morphology of the layers. Indeed, the layers grown from tBASe showed a significant improvement in thickness uniformity and surface roughness in comparison with the films grown from hydrogen selenide under similar conditions.[10] The pyrolysis study showed that DMZn in the presence of tBASe decomposes at significantly lower temperatures than pure DMZn in hydrogen gas.[21] On the other hand, the decomposition of tBASe seems to be affected only slightly by the presence of DMZn. Thus, the decomposition of the codosed DMZn is likely initiated by the reactive intermediates formed by pyrolysis of tBASe. This result is consistent with the OMCVD experiments when tBASe was found to be the growth limiting reagent in the kinetically controlled growth regime.[10]

A gas-phase mechanism accounting for the formation of the selenium containing byproducts is shown in Scheme 2. Allylselenium radicals, formed by pyrolysis of tBASe, can recombine with allyl radicals to form DASe or with methyl radicals to yield MASe. At temperatures above ~400 °C MASe decomposes to a methylselenium radical,[7] which may recombine with another methyl radical to yield the observed DMSe. The pathways leading to the allylselenium byproducts compete for allylselenium radicals with DMZn or methyl zinc radicals. This reaction channel results in deposition of ZnSe and liberation of allyl radicals. Recombination reactions of allyl radicals accounts for the presence of 1,5-hexadiene and hydrogen abstraction for the formation of propene.

To grow ZnSe with a low carbon level, the side reactions of allylselenium radicals leading to DASe and

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(21) Patnaik, S.; Jensen, K. F., unpublished results.

Scheme 2. Mechanism of Formation of Selenium-Containing Byproducts for Copyrolysis of tBASe and DMZn[a]
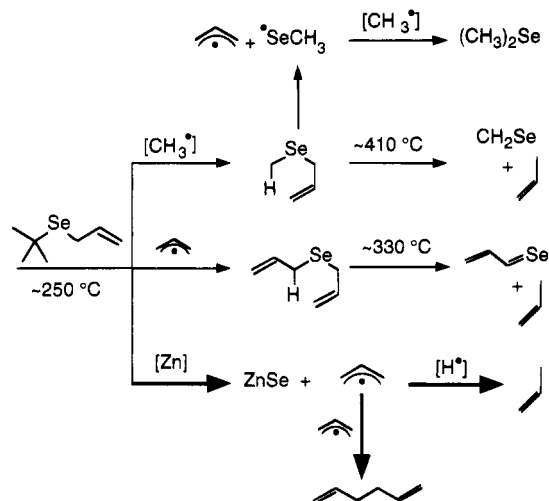
[a] The major low-temperature reactions are shown with bold arrows. The symbols [H·] and [CH₃·] stand for hydrogen radical and methyl radicaldonors, respectively. The symbol [Zn] represents zinc bearing species, such as (CH₃)₂Zn, CH₃Zn·, and elemental zinc.

MASe have to be reduced. Low partial pressures of the precursors and a short reactor residence time are important growth parameters which can be used to control these unwanted side reactions. The most undesirable byproduct is DASe since even low concentrations of this species in the gas phase may result in an extensive carbon incorporation.[10] Fortunately, the formation of DASe is significantly reduced in the presence of DMZn due to the competing reactions resulting in formation of MASe and ZnSe deposition. Thus, low VI/II ratios in the gas-phase may be used to control the concentration of DASe. Deposition temperature is also an important operating parameter in controlling the carbon concentration in the film because tBASe decomposes at significantly lower temperatures than DASe and MASe. Moreover, since the higher reactivity of tBASe leads to higher growth rates,[10] contributions of allylselenium to the growth should be marginal at low growth temperatures (below ~400 °C).

Conclusion

The pyrolysis study in combination with previous OMCVD experiments[10] showed that tBASe is a successfully designed precursor for low temperature growth of ZnSe. The retro-ene pyrolysis pathway, typical for DASe and MASe, is not available for tBASe, and the films show negligible carbon contamination, typically below the detection limit of SIMS of ~5 × 10^17 atoms/cm³. A complex pyrolysis mechanism of the heteroleptic precursor complicates the growth chemistry with the formation of DASe and MASe byproducts. To reduce the extent of the side reactions, which potentially can affect the quality of the deposited layers, the OMCVD growth has to be carried out at a low temperature, low partial pressures of the precursors, low VI/II ratios, and a short reactor residence time. Such growth conditions are also desirable for synthesis of uniform layers with a low density of structural defects.

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