

Mechanistic Studies of the Chemical Vapor Deposition of Ceramic and Metal Films from Organometallic Precursors

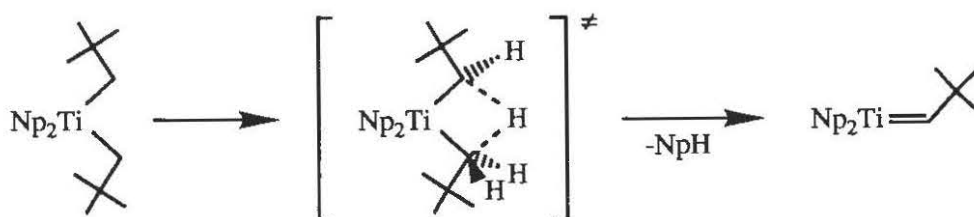
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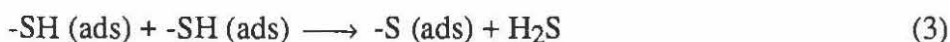
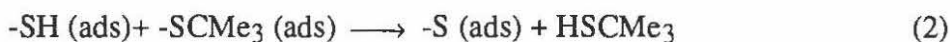
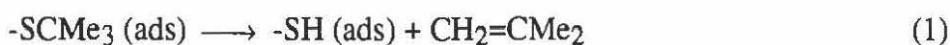
For the past three decades, metal-organic chemical vapor deposition (MOCVD) methods have been increasingly employed for the preparation of thin film devices due to the low deposition temperatures, high growth rates, high purities, and ease of process control characteristic of this technique [1-10]. Although there are many studies of the preparation of new precursors and their conversion to thin films via MOCVD routes, mechanistic studies have been quite few [11-19]; in many cases the decomposition pathways including surface reactions are still completely unknown. A better understanding of the decomposition pathways is necessary in order to develop better organometallic precursors and to improve and extend MOCVD techniques.

In 1987, a MOCVD method for the low-temperature deposition of amorphous titanium carbide (TiC) thin films from tetra(neopentyl)titanium (TiNp_4) was described [20, 21]. Mechanistic studies of the thermolysis of TiNp_4 in solution in parallel with studies of the chemical mechanism responsible for its conversion to titanium carbide under CVD conditions have now been carried out [22, 23]. In hydrocarbon solutions, the neopentyl complex thermolyzes to eliminate 2.1 equiv of neopentane as the principal organic product. A deuterium kinetic isotope effect ($k_{\alpha(\text{H})}/k_{\alpha(\text{D})} = 5.2 \pm 0.4$) upon deuterating the alkyl groups at the α positions provides clear evidence that the initial step in the thermolysis is an α -hydrogen elimination reaction to form neopentane. The activation parameters for this α -hydrogen elimination process are $\Delta H^\ddagger = 21.5 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -16.6 \pm 3.8$ cal/mol K. The titanium-containing product of this reaction is a titanium alkylidene, which in solution activates C-H bonds of both saturated and unsaturated hydrocarbon solvents such as benzene and cyclohexane. No activation of the C-F bonds of hexafluorobenzene is seen, however.



The chemical pathway responsible for the conversion of TiNp_4 to TiC has been studied under chemical vapor conditions and on single crystals in ultra-high vacuum [23]. For every equivalent of TiNp_4 consumed in the deposition process, 3.25 equiv of neopentane and 0.16 equiv of isobutane are produced; other organic species are also formed but in relatively small amounts. Thermolysis of the specifically deuterated analogue $\text{Ti}(\text{CD}_2\text{CMe}_3)_4$ yields a 2.25:1 ratio of neopentane- d_3 and neopentane- d_2 ; this result combined with a kinetic isotope effect of 4.9 at 385 K shows that the first step in the deposition pathway under CVD conditions is α -hydrogen elimination. The α -hydrogen elimination step produces one equivalent of neopentane and a titanium alkylidene, which undergoes further α - (and eventually γ -) hydrogen activation processes to generate the second and third equivalents of neopentane. In the last stages of the thermolysis sequence, neopentyl (or neopentyl-derived) organic groups evidently fragment and generate the carbon atoms that eventually form the titanium carbide phase.

Molybdenum disulfide is of interest as a solid lubricant for high precision space borne applications [24] and for the fabrication of efficient solar energy cells [25]. Similarly, titanium disulfide is of interest because it is one of the most effective cathode materials in high energy, rechargeable batteries [26], and also can serve as a solid lubricant [27]. The deposition of amorphous MoS₂ and TiS₂ thin films from the metal-organic precursors Mo(S-*t*-Bu)₄ and Ti(S-*t*-Bu)₄ has been investigated [28]. Stoichiometric films nearly free of oxygen and carbon contaminants can be grown at temperatures between 110 and 350 °C and low pressure; for TiS₂, the deposition apparatus was treated with TiCl₄ before the deposition runs to remove adventitious water and reduce the amount of oxygen impurities. The organic by-products generated during deposition consist principally of isobutylene and *tert*-butylthiol; smaller amounts of hydrogen sulfide, di(*tert*-butyl)sulfide, and di(*tert*-butyl)disulfide are also generated. A β-hydrogen elimination/proton transfer mechanism accounts for the distributions of the organic byproducts seen during the deposition of MoS₂ and TiS₂ films.



Zinc-containing group II/VI semiconducting thin films have been shown to be useful as the key components in optoelectronic devices such as light emitting diodes and solar cells [1-2, 4]. The organometallic compounds bis(allyl)zinc and bis(2-methylallyl)zinc have been investigated as MOCVD precursors for the deposition of zinc at temperatures as low as 150 °C [29]. The deposits consist of aggregates of hexagonal plates and columns. Analyses of the organic byproduct distribution and *in situ* spectroscopic studies on single crystal Cu(111) surfaces show that bis(allyl)zinc adsorbs molecularly at temperatures below 200 K, but that the allyl groups transfer to the copper surface at 250 K; the surface-bound allyl groups are bound in a trihapto fashion. On fresh surfaces, the allyl groups fragment to adsorbed hydrogen atoms and hydrocarbon fragments; the former react with intact allyl groups to give propene while the latter eventually give rise to a carbonaceous overlayer. Once the overlayer is formed, fragmentation of allyl groups is inhibited and, instead, coupling of allyl groups to 1,5-hexadiene is the predominant reaction channel. Passage of a mixture of bis(2-methylallyl)zinc and bis(2-methylallyl)palladium over substrates at 250 °C and 10⁻² Torr results in the deposition of Zn/Pd alloys.

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