# Low Temperature Deposition of Metal Nitrides by Thermal Decomposition of Organometallic Compounds

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## ABSTRACT

Decomposition reaction of dialkylamides of boron, silicon, tin, titanium, zirconium, niobium, and tantalum was investigated. The amides of transition metals decomposed to the corresponding nitrides at 300°-500°C, whereas those of boron, silicon, and tin yielded elemental deposits at higher temperatures. In the deposition of titanium nitride from titanium tetrakis(dimethylamide), two optimum temperatures at 400° and at 800°C in nitrogen or hydrogen atmosphere were found, but in argon only low temperature deposition was possible. The low and high temperature processes are discussed in relation to mass spectral analysis of the exhaust gases formed at various decomposition temperatures.

Metal nitrides are well known to have outstanding physical and chemical properties and have been prepared by the reactions of metal halides or hydrides with nitrogen + hydrogen or ammonia, or of metals with nitrogen (1). These reactions usually require temperatures higher than  $1000^{\circ}$ C, which have limited the application of the nitrides as the useful coatings on many materials. Therefore, their preparation at lower temperature, where deformation of substrate materials can be avoided, should be important.

Recently, the use of organometallic compounds as the starting materials for the vapor deposition of some inorganic compounds such as oxides has been reported (2). Dialkylamides of metals are of particular interest with respect to the fact that they have direct metalnitrogen  $\sigma$ -bonds, and controlled thermal decomposition of these organometallics could result in the deposition of the corresponding nitrides at temperatures much lower than the conventional preparation techniques mentioned above. With this in mind, the thermal decomposition of dialkylamides of various metals is investigated, and a detailed examination of the decomposition products including organic compounds was performed using titanium tetrakis (dimethylamide) as a representative compound.

#### Experimental

Materials—Metal dialkylamides used in this study were prepared according to the modified method of literature (3) from lithium dialkylamides and the corresponding metal chlorides and were supplied to be used for the decomposition reaction after identification with infrared, NMR, and mass spectra (4). Silicon tetrakis(dimethylamide) was found to include about 75% of chlorotris(dimethylamino)silane but was used without further isolation. Argon, hydrogen, and nitrogen were refined by passing over titanium sponge heated at *ca.* 800°C and phosphorus pentoxide, successively. Helium and other Guaranteed Grade reagents were used without further purification.

Decomposition reaction of the amides—An apparatus used for the decomposition reactions is shown in Fig. 1. An amide saturated in a carrier gas (argon, hydrogen, or nitrogen) at a suitable temperature, where it is thermally stable (in most cases below 100°C except for silicon amide; 140°C), was introduced onto a substrate [about 10  $\times$  10 mm<sup>2</sup>: quartz, graphite, stainless steel (Ni 18, Cr 8), or copper plate] which was mounted on a SiC heater in a reaction tube (quartz; inside diameter 25 mm). The reactor was cooled by water flow from the outside in order to avoid the deposition on its inside surface. Temperature of the substrate was measured by an Alumel-Chromel

Key words: metal-dialkylamides, nitrides, thermal decomposition.

thermocouple (uncorrected) and was regulated using a regulator (Chino Electric Company, Model E-500). After the decomposition reaction, the furnace was cooled in an atmosphere of flowing carrier gas to room temperature. Most substrates were used after polishing with an emery paper. The surface of the copper plate was cleaned by heating in air and subsequent steeping in methanol. The films on the substrate were examined *in situ* on the substrate by x-ray diffraction (Rigaku Electric Company, Type 2040), scanning electron microscopy (JEOL, Model U3), and partly by x-ray microprobe analysis (JEOL, Model JAX-5 CHD).

Analysis of the exhaust gas—The exhaust gas formed in the decomposition of an amide was analyzed by gas chromatography (F.I.D.; Apiezon L column, 1.0m;  $20^{\circ}$ C) and by bubbling through a benzene solution of naphthylisocyanate which reacts to form urea derivatives of the corresponding amines. Detailed analysis was performed by a mass spectrometry. Helium gas, which was used because it does not interfere with detection of fragments with low molecular weights, was saturated with the vapor of titanium tetrakis(dimethylamide) or the silicon analogue and was passed through a quartz furnace (inside diameter 15 mm) heated from the outside at a given temperature. The gas formed was first collected in a gas reservoir, before it was introduced into the spectrometer (JEOL, JMS-01SG).

Evaluation of quantity of vapor transported of titanium tetrakis(dimethylamide).—Titanium amide is so sensitive to moisture and oxygen that it is difficult for us to determine the quantity transported by a



Fig. 1. Schematic diagram of the apparatus used for the decomposition of amides. 1, Substrate; 2, SiC heater; 3, carbon powder; 4, graphite; 5, iron rod; 6, a-c thermocouple; 7, amide saturator; 8, flow meter; 9, titanium sponge; 10, Nichrome heater.

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carrier gas. However, this compound has been reported to react with carbon disulfide giving the stable complex, titanium tetrakis(N.N-dimethyldithiocarbamate) (5). Thus, by bubbling the carrier gas (nitrogen) saturated with the titanium amide at 90°C into a benzene solution of carbon disulfide and collecting the red precipitates by filtration, the quantity of the amide transported was calculated from the weight of the precipitates as 0.032 mg/ml (N<sub>2</sub>).

# Results

Decomposition products .- When the vapor of titanium tetrakis(dimethylamide) saturated in nitrogen gas was introduced onto a quartz substrate which was heated at 400°C, it decomposed resulting in brownish coatings. Their x-ray diffraction showed broad peaks, which are fully consistent with those of titanium ni-tride as shown in Fig. 2. The peaks became more pronounced when annealed in argon atmosphere at 800°C for 10 min. The high temperature decomposition products were yellow-colored and had sharper x-ray diffraction peaks (see Fig. 2). The low and high temperature products were inert to hydrochloric acid and sulfuric acid but were etched partly by nitric acid and soluble in aqua regia, being consistent with the chemical properties of titanium nitride. The x-ray microprobe analysis of the product obtained at 400°C shown in Fig. 3 suggests a homogeneous nitride which contains a small quantity of carbon, particularly in the grain boundaries. The lowest formation temperature was about 250°C.

The decomposition reaction was evident in hydrogen as well as in nitrogen. On the other hand, in argon atmosphere the nitride deposition was observed analogously at lower temperature reaction (about 400°C) but was very poor at temperatures higher than 700°C.

The decomposition reaction of other amides was investigated in a similar manner, and the products are listed in Table I, together with their lowest forma-tion temperatures. The amides of transition metals such as titanium, zirconium, and niobium gave the corresponding nitrides. Their x-ray diffraction patterns are reproduced in Fig. 2. Tantalum amide gave the grayish deposits which had x-ray diffraction peaks Cu-K $\alpha$  2 $\theta$  = 36.2°, 41.9°, and 61.0° (relative intensity 100:70:30) which were not consistent with available data of tantalum compounds. Therefore, we could not identify the products.

On the other hand, amides of boron and tin did not yield a nitride at any temperature in the range 300°-1000°C but gave the elements themselves. Boron was obtained above 700°C in the brown films and was identified by x-ray diffraction and the easy dissolution in nitric acid. Tin was formed at  $300^{\circ}$ - $1000^{\circ}$ C as gray coatings, which were clearly identified by the x-ray diffraction analysis (30.2°, 31.6°. 43.5°, and 44.5°). In the decomposition of silicon amide which was found to consist of both silicon tetrakis(dimethylamide) and monochloride(nearly 1:3, see experimental section), white powder and homogeneous yellowish or brownish coating were obtained at 800°C, below which no depositions occurred. The



Fig. 3. X-ray microprobe analysis of the deposits obtained from Ti(NMe<sub>2</sub>)<sub>4</sub> on quartz at 400°C in nitrogen.

former was identified as ammonium chloride by infrared spectrum and x-ray diffraction. The latter adhered tightly on the quartz substrate and exhibited no x-ray diffraction peaks, indicating an amorphous material. Its infrared spectrum showed the presence of an aminogroup  $(v_{N-H} \ 1400 \ cm^{-1})$  (6). Its further heating at a higher temperature (1100°C) in argon released a small quantity of ammonia, suggesting that the de-posit contained silicon amide. It was oxidized gradually in air at 1300°C to give a blue-colored product. In figuring the weight increase after the oxidation, silicon content in the product was estimated to be at least 80%. It was soluble partly in hydrofluoric acid, partly in 20% sodium hydroxide, and partly in hydrofluoric acid + nitric acid. Therefore, it can be assumed that the brownish product from silicon alkylamide contains a few compounds such as silicon, silicon nitride (or amide), and silicon carbide. But, the result of the oxidation reaction strongly suggests that silicon is a major product. Thus it is of great interest that the decomposition of the amides of the main group elements has a tendency to result in the corresponding elements themselves rather than the nitrides, being in striking contrast to that of transition metal amides.

Table I. Metal dialkylamides, decomposition products, and the lowest formation temperatures of nitrides



Fig. 2. X-ray diffractions of deposits formed on quartz

Temperature dependence of deposition .-- The lowest formation temperatures of nitrides shown in Table I are remarkably low compared with those in the conventional chemical vapor depositions. The amides hav-ing a higher molecular weight or of heavier elements are apt to decompose at higher temperatures. The temperature dependence of the deposition was studied in more detail using titanium tetrakis(dimethylamide) and tetrakis(diethylamide) as representative compounds. The results in nitrogen are shown in Fig. 4 and 5, respectively. The maximum yields were found at about 400°-500°C and at a temperature above 800°C in either compounds, when hydrogen or nitrogen was used as a carrier gas. In the case of argon carrier, however, the nitride deposition occurred analogously at lower temperatures but was extremely suppressed at higher temperatures. The titanium nitride content in the deposits was evaluated from titanium oxide  $(TiO_2)$ formed by oxidation in air, and is shown also in Fig. 4 and 5. These results strongly suggest that the different mechanisms can take part in the low and high temperature decompositions. Table I indicates that the amides of the main group elements gave deposits at higher temperatures than those of transition metals.

Analysis of the exhaust gases.—In order to clarify the processes of deposition, the exhaust gas of the decomposition reaction was examined by gas chromatography, mass spectroscopy, and chemical analysis. When the exhaust gas formed by the decomposition of titanium tetrakis(dimethylamide) at the optimum condition ( $400^{\circ}$ C) in nitrogen was bubbled into a benzene solution of naphthylisocyanate, white crystals which were identified as pure dimethylnaphthylurea by NMR and infrared spectra, m.p. and thin layer chromatography were separated, indicating a selective formation of dimethylamine. Its yield was found to decrease with the increasing decomposition temperature. The gas chromatographic analysis showed at least three peaks, one of which was identified as dimethylamine.

Detailed analysis of the gases obtained at the decomposition temperatures  $300^{\circ}$ ,  $600^{\circ}$ , and  $800^{\circ}$ C in helium atmosphere was performed using a mass spectroscopy, and the results are shown in Fig. 6, in which the relative intensities of fragments to a fragment m/e 78 (unidentified) are shown. This figure indicates that at lower temperatures the elimination of dimethylamine was dominant and that at temperatures above  $600^{\circ}$ C further degradation could take



Fig. 4. Temperature dependence of deposition and purity from  $Ti(NMe_2)_4$  on quartz in nitrogen.



Fig. 5. Temperature dependence of deposition and purity from  $Ti(NEt_2)_4$  on quartz in nitrogen.



Fig. 6. Mass spectral analysis of the exhaust gases formed in the decomposition of  $Ti(NMe_2)_4$  at different temperatures.

place. The formation of hydrogen and methane became significant at  $800^{\circ}$ C, which indicates an occurrence of a full decomposition of the complex. In contrast, the deposition yields of titanium nitride were maximum at about  $400^{\circ}$ C and at a temperature higher than  $800^{\circ}$ C, and a minimum of  $600^{\circ}$ C (see Fig. 4 and 5).

The temperature dependence of the composition of the exhaust gas of silicon dimethylamide was similar to that of titanium dimethylamide, as shown in Fig. 7. In the case of silicon amide, however, the deposition was found only at a temperature above  $700^{\circ}$ C. The difference between the behavior of silicon and titanium amides may be related to the stability of an intermediate of the reaction. The main fragments in the mass spectra of silicon and titanium complexes are summarized in Table II. In the case of the former, bis (dimethylamino) siliconium ion was observed at high abundance, but the analogous fragment ion of titanium was absent, suggesting the higher stability of low valent silicon species.



Fig. 7. Mass spectral analysis of the exhaust gases formed in the decomposition of  $Si(NMe_2)_4$  [includes 75% of  $ClSi(NMe_2)_3$ ] at different temperatures.

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Fig. 8. TiN deposits formed on quartz. A, 300°C, low deposition; B, 300°C, high deposition; C, 800°C; D, 1000°C).

Properties of deposits .-- In Fig. 8, the scanning electron micrographs of a typical titanium nitride deposited on a quartz substrate are shown. The grain sizes of the nitride obtained at a lower temperature were larger than those at a higher temperature. The x-ray diffraction pattern of low temperature deposits was quite similar to that of powdered titanium nitride except for considerable broadening, but the high temperature deposits had a larger intensity of (111) peak (see Fig. 2). Figure 8 demonstrates that the high temperature deposits are partly crystallized.

The deposition onto some other substrates such as graphite, copper, and stainless steel was also examined. The deposition rates on these substrates were found to be  $0.25 \text{ mg/cm}^2 \cdot \text{min}$  (about 15% yield for the amide introduced), thus being faster than on the quartz substrate (0.15 mg/cm<sup>2</sup>·min). This difference might be due to the thermal conductivity of the substrates rather than their chemical nature such as a catalytic action of the surfaces. The adherence of the deposits to graphite and copper substrates seemed preferable to that of stainless steel and quartz. The deposits on the two latter substrates were often found to peel off. A cross section of the titanium nitride deposited on a quartz at 300°C is shown in Fig. 9. At the inter-

Table II. Mass spectra of  $M(NMe_2)_4$  (M = Si and Ti)\*

Fragment ion**	Intensity (%)	
	Si	Ti
M(NMe <sub>2</sub> ) <sub>4</sub>	44.7	22.0
[M(NMe <sub>2</sub> ) <sub>3</sub> Cl]†	[66.0]	
[M(NMe <sub>2</sub> ) <sub>3</sub> ]†	[55.3]	
M(NMe <sub>2</sub> ) <sub>2</sub> NMeCH <sub>2</sub>	13.8	8.0
M(NMe <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub>	2.4	13.5
M(NMe <sub>2</sub> ) <sub>2</sub>	20.2	—
Me <sub>2</sub> NH	100.0	100.0

Measured at 20 eV.
 These formulas were assigned from the high resolution analysis using perfluorokerosene as an internal standard (errors are within 5 mmass).
 † Molecular ion of chlorotris(dimethylamino)silane involved and a fragment ion formed by its fragmentation.

face between the nitride and the surface of the quartz, no other layers were found, suggesting that the nitride did not react with quartz at the deposition condition. The color of the nitride was brownish or dark yellowish at low temperature but became yellowish at a high temperature, being similar to the appearance of a typical titanium nitride.

A qualitative electrical conductivity measurement (four terminal method) showed that the nitride had a resistivity  $10^{-2}$  ohm cm at room temperature, which is not in agreement with that of normal nitride (21.7  $\times$  10<sup>-6</sup> ohm cm) (7), probably due to imperfect coatings, the contamination of some impurities (in particular at the grain boundaries), and the existence of fine cracks.

## Discussion

The deposition processes of metal nitrides from the corresponding amides can be expected to vary with temperature. At low temperature, the deposition was independent of the atmosphere, but at high temperature, the process was affected by the atmospheric gas, and the deposition was suppressed in argon. Mass spectral results of the exhaust gas indicated that the



Fig. 9. Cross section of TiN films deposited on quartz at 300°C

low temperature decomposition gave mainly amine, but the high temperature caused a full degradation of complexes. Therefore, the following decomposition schemes might be assumed

Unfortunately it was difficult to obtain a perfect homogeneous coating over the surface of the substrates even when the careful experiments were performed, probably due to very low thermal stability of the

Low temperature: 
$$M(NMe_2)_4 \longrightarrow M(NMe_2)_3 \longrightarrow M(NMe_2)_2 \longrightarrow MN_x$$
  
High temperature:  $M(NMe_2)_4 \longrightarrow Metal species + \begin{cases} H_2 \text{ and/or} \\ N \text{ compounds} \end{cases}$ 

In the low temperature process, the amides may decompose through a successive elimination of amine fragments to give a low valent metal amide, followed by subsequent elimination of alkyl groups to yield the corresponding nitrides. A nitrogen atom originally bound to the metal may remain in the product without any separation through the reaction. Meanwhile, at high temperatures a complete degradation of the amides is preferable, followed by a recombination of metallic species formed with nitrogen compounds or by a further reduction with hydrogen, affording the nitrides. When argon is used in this reaction, it may dilute the concentration of nitrogen species or hydrogen to make the formation of the nitrides difficult. In a hydrogen atmosphere, splitting of the N-C bonds may be accelerated. These tentative schemes can explain the existence of two maxima in the temperature dependence of deposition. The optimum conditions were concluded to exist at approximately 400°C and at a temperature higher than 800°C in low and high temperature depositions, respectively.

At a medium temperature (about 600°C), the complete decomposition may take place, but this temperature is too low for nitride formation by subsequent recombination reactions. The amides of a main group elements may be so thermally stable that the successive reaction is difficult to occur. Therefore, they can decompose only at a high temperature to the elements. This selective element formation (the representative case was tin from tin dimethylamide) may be attributed to the easy reduction of the amides to zero valent species in comparison to the transition metals such as titanium.

In the case of titanium, zirconium, and niobium compounds, the corresponding nitrides which contain a small quantity of carbon were obtained. Although the product from the tantalum amide could not be identified, it is supposed that it is to be a kind of nitride. In spite of a larger ratio of carbon to nitrogen in the starting materials the selective formation of nitrides suggests that the nitrogen atoms originally linked are important for it, although the thermodynamic data also indicate the nitride formation to be easier than the carbide (8).

amides. However, this defect may be corrected in a procedure of reduced reaction pressure.

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