# Deposition of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> Films via Pyrolysis of Aluminum Acetylacetonate and Hexamethyldisiloxane in the Presence of Nitrogen Compounds

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**Abstract**—Kinetic measurements were used to assess the effects of  $N_2O$ , NO, and diethylamine on the chemical vapor deposition of  $SiO_2$  films on Si from hexamethyldisiloxane and the effect of diethylamine on the deposition of  $Al_2O_3$  films on Si, GaAs, and InP from aluminum acetylacetonate. The composition of the films was determined by electron probe x-ray microanalysis and Auger electron spectroscopy. The deposition kinetics and properties of the films are correlated with the nature of the gaseous admixture and process parameters.

## INTRODUCTION

The preparation of high-quality oxynitride films on silicon is of practical importance in semiconductor technology. The major approaches to producing oxynitride films are chemical vapor deposition (CVD) at low or atmospheric pressure and thermal nitridation of silica. The former approach involves pyrolysis of gas mixtures typically containing SiH<sub>4</sub> (or SiH<sub>2</sub>Cl<sub>2</sub>), NH<sub>3</sub>, and N<sub>2</sub>O (or NO) [1, 2]. The latter consists in heat treatment of silicon or silica in NH<sub>3</sub>, NO, N<sub>2</sub>O, or N<sub>2</sub> vapor [3, 4]. The use of nitrogen oxides for thermal oxidation of silicon gives rise to changes in the deposition mechanism, composition, and structure of the films and improves their dielectric properties.

The effect of amines on the growth rate and properties of  $SiO_2$  and  $Al_2O_3$  films being deposited from aluminum acetylacetonate and hexamethyldisiloxane (HMDSO) [5, 6] is of great interest. First, because amines are carrier killers: upon decomposition, they recombine with the radicals resulting from the destruction of organoelement compounds, thereby suppressing further decomposition of the radicals, which might otherwise result in contamination of the growing film with carbon [7]. Second, diethylamine is a nitrogen source, and its reaction with aluminum acetylacetonate or HMDSO may lead to the incorporation of nitrogen into the film and formation of an oxynitride layer.

In developing new approaches to producing oxynitride layers with controlled properties, it is expedient to extend the range of suitable Si compounds and also to assess the effects of nitrogen-containing gaseous admixtures on the growth, composition, and properties of the films. The purpose of this work was to investigate the CVD of oxide films on Si substrates via HMDSO pyrolysis in the presence of  $N_2O$ , NO, or diethylamine and also on Si, GaAs, and InP substrates via pyrolysis of aluminum acetylacetonate in the presence of diethylamine.

### **EXPERIMENTAL**

In our preparations, we used commercial  $N_2O$ ; NO was prepared as described in [8]. KDB (B-doped) Si(100) wafers ( $\rho = 7.5 \Omega$  cm) were cleaned by standard peroxide-ammonia cycles [9]. HMDSO (reagent grade) was additionally purified by sublimation. CVD was carried out in a resistance-heated horizontal quartz reactor. The temperature was controlled with an accuracy of  $\pm 2^{\circ}$ C. HMDSO was transported to the substrate by an argon carrier flow at 25°C through a bubbler. The argon flow rate was adjusted so that the HMDSO concentration in the gas phase was constant. The gas phase contained, along with HMDSO and argon, N<sub>2</sub>O (GP 1),  $air + N_2O$  (GP 2), NO (GP 3), air + NO (GP 4), diethylamine (GP 5), or air (GP 6). Al<sub>2</sub>O<sub>3</sub> films were deposited using aluminum acetylacetonate synthesized and purified as described in [5]. Diethylamine was used without dilution or was mixed with water (4.1 mol/l). To assess the effect of diethylamine on the deposition rate, composition, and properties of Al<sub>2</sub>O<sub>3</sub> films, we used two approaches, either introducing diethylamine vapor into the gas phase during the pyrolysis of aluminum acetylacetonate or annealing as-deposited films in diethylamine vapor. Deposition was carried out at 400°C in a resistance-heated furnace. The temperature was maintained with a stability of  $\pm 2^{\circ}$ C. Aluminum acetylacetonate was contained in a cylinder at 250°C. The flow rate of argon carrier gas was 3 l/h. The tem-

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**Fig. 1.** Film thickness as a function of deposition time for  $Al_2O_3$  deposited on (1, 4) InP, (2, 5) Si, and (3, 6) GaAs substrates via pyrolysis of aluminum acetylacetonate at 400°C (4–6) in the presence of diethylamine (7.5 × 10<sup>-2</sup> mol/h) and (1–3) without it.

perature of the diethylamine source was 70°C.  $Al_2O_3$ was deposited on KDB Si(100) ( $\rho = 7.5 \ \Omega \ cm$ ), SAGOCh GaAs(100) (carrier concentration,  $10^{16} \ cm^{-3}$ ), and FIE-1 InP(100) ( $2 \times 10^{15} \ cm^{-3}$ ) substrates.

The film composition was determined by electron probe x-ray microanalysis (EPXMA). Composition– depth profiles were obtained by Auger electron spectroscopy (AES) with an IOS-10-005 instrument during Ar<sup>+</sup> ion milling. Film thicknesses were measured with an LEF-3M ellipsometer to an accuracy of  $\pm 1$  nm. The IR spectra of the films were recorded with a UR-10 Carl Zeiss spectrophotometer.

### **RESULTS AND DISCUSSION**

The kinetics of  $Al_2O_3$  deposition on Si, GaAs, and InP substrates with and without diethylamine were found to follow a linear rate law (Fig. 1). The deposition rate was independent of substrate material and was

**Table 1.** Thicknesses and indices of refraction of the  $Al_2O_3$ films on Si before and after annealing in an argon + diethy-lamine mixture at 400°C for 10 min

d, nm		n		
before annealing	after annealing	before annealing	after annealing	
50	50	1.78	1.66	
114	107	1.56	1.55	
114*	110*	1.56*	1.55*	
200	167	1.58	1.56	

\* Annealing without diethylamine.

1.8 times faster in the presence of diethylamine. The index of refraction, *n*, of the films produced in the presence of diethylamine was somewhat higher than that of the films grown in oxygen and argon without diethylamine and varied, depending on the deposition duration, in the ranges 1.58–1.66, 1.64–1.66, and 1.57–1.64 for the Si, InP, and GaAs substrates, respectively. The index of refraction of the films deposited on Si, InP, and GaAs without diethylamine was 1.57–1.59, 1.61–1.64, and 1.54–1.55, respectively.

The thicknesses and indices of refraction of the  $Al_2O_3$  films annealed in the presence of diethylamine at 400°C for 10 min are listed in Table 1.

To examine the possibility of enhancing the nitrogen content of Al<sub>2</sub>O<sub>3</sub> films on Si, the films were annealed between 400 and 600°C for 1 h in the presence of diethylamine vapor. The results are summarized in Table 2. The compositions of the films deposited via pyrolysis of aluminum acetylacetonate in the presence of diethylamine and without it are listed in Table 3. The average A1 : O atomic ratio in the films produced in oxygen + argon mixtures is 3:5, and that in the films deposited in the presence of diethylamine is 3:2. As is well known, thermal decomposition of metalorganic (MO) compounds may occur both on the substrate surface and in the gas phase [5]. Gas-phase reactions are more likely near the decomposition temperature and at higher concentrations of the MO compound. Besides, the probability of gas-phase decomposition is higher for less stable and volatile compounds. It would be expected that the introduction of admixtures into the gas phase might also have a significant effect on the dynamic equilibrium between the gas phase and the growing film. Reactions between MO and nitrogencontaining compounds can follow two, distinctly different paths: decomposition of the MO compound to the metal, which then reacts with the admixture to form a nitride, or radical substitution yielding an intermediate compound already containing bonds necessary for film formation. Increasing the difference in redox potential between the MO and nitrogen-containing compounds favors heterolytic substitutions in MO compounds [5]. It may be that, in the presence of dieth-

**Table 2.** Effect of annealing temperature (diethylamine vapor, 1 h) on the thickness and index of refraction of  $Al_2O_3$  films on Si

t <sub>ann</sub> , °C	<i>d</i> , n	m	n		
	before annealing	after annealing	before annealing	after annealing	
400	60	60	1.59	1.69	
450	104	91	1.58	1.78	
510	107	93	1.58	1.79	
600	68	57	1.58	1.79	

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**Fig. 2.** Film thickness as a function of deposition time for  $SiO_2$  deposited on Si via pyrolysis of HMDSO (1.4 mol/h) at 750°C (1) in the presence of diethylamine (7.5 ×  $10^{-2}$  mol/h) and (2) in air (31 l/h).

ylamine, radical substitutions in aluminum acetylacetonate lead to the formation of an intermediate aluminum compound containing Al–N bonds. However, we found no nitrogen in the films, which were enriched in aluminum. This finding, together with the fact that the deposition kinetics were independent of substrate material, leads us to assume that the reaction rate is controlled by a gas-phase process. Moreover, the films deposited in the presence of diethylamine contained no carbon, presumably because of the aforementioned suppression of secondary radical decomposition, preventing contamination with carbon.

The kinetics of SiO<sub>2</sub> growth on Si via pyrolysis of HMDSO both in the presence of diethylamine and without it followed a parabolic rate law (Fig. 2). The introduction of diethylamine into the gas phase (GP 1) reduced the growth rate of SiO<sub>2</sub> on Si in comparison with deposition in air (GP 2) (Fig. 3). The decrease in growth rate with increasing temperature or on the addition of an admixture is likely to be associated with a reduction in the time span between adsorption and reaction events or a reduction in the effective density of surface sites. The lower growth rate in the presence of diethylamine can be accounted for under the assumption that the reaction of HMDSO with diethylamine occurs in the gas phase, as in the case of aluminum acetylacetonate. The indices of refraction of the films deposited from GP 1 were higher, presumably because of the formation of oxynitride layers.

This assumption is supported by AES data (Fig. 4). The films deposited at different temperatures all contain nitrogen. In the films produced between 650 and 750°C, the carbon content is fairly high in the surface



**Fig. 3.** (1, 2) Growth rate and (3, 4) index of refraction vs. temperature for SiO<sub>2</sub> deposited on Si via pyrolysis of HMDSO ( $1.4 \times 10^{-2}$  mol/h) (2, 3) in air and (1, 4) in the presence of diethylamine ( $0.4 \times 10^{-2}$  mol/h).

layer and rapidly decreases with depth, whereas the carbon content of the film deposited at 800°C is high throughout the film thickness. Free Si is missing in the top layer, but its content rises deeper into the film, passes through a flat maximum at half thickness, then drops sharply, and rises again at the film–substrate interface. The content of silicon bonded to oxygen rises with depth in all of the films studied, and at the interface all of the silicon is coordinated by oxygen. The presence of free silicon seems to be due to the redox process  $2SiO \longrightarrow SiO_2 + Si$ . Concurrently, the oxygen incorporated into the film oxidizes silicon:  $\frac{1}{2}Si + xO_2 \longrightarrow \frac{1}{2}SiO_x$ . As evidenced by depth profiling

data, most of the silicon combines with oxygen to form a nonstoichiometric oxide. The presence of nitrogen testifies to radical substitution reactions yielding an

**Table 3.** Elemental composition (at. %) of  $Al_2O_3$  films produced by aluminum acetylacetonate pyrolysis in air + argon and argon + diethylamine mixtures (EPXMA data)

Substrate	Gas phase	<i>d</i> , nm	Al	0	С
Si	Air + argon	505	34.8	62.1	3.1
GaAs	"	831	37.6	60.1	2.2
InP	"	759	37.5	60.4	2.1
Si	Argon + diethylamine	303	63.3	36.7	-
GaAs	"	297	60.7	39.3	-
InP	"	322	56.5	43.5	-



**Fig. 4.** AES depth profiles of films deposited on Si via HMDSO pyrolysis in the presence of diethylamine at (a) 650, (b) 700, (c) 750, and (d) 800°C; deposition time, 10 min; (*I*) N, (*2*) C, (*3*) free Si, (*4*) combined Si, (*5*) O.

intermediate organosilicon compound containing Si–N bonds, which then converts into the final product. The low nitrogen content of the films and the reduced growth rate in the presence of diethylamine suggest that the reaction between diethylamine and HMDSO occurs in the gas phase. The resulting molecular fragments decompose further on the substrate surface. Judging from the sharp decrease in carbon content in the nearsurface region, this process is accompanied by breaking of Si–C bonds in the molecular fragments and carbon removal in the form of volatile compounds.

Figure 5 displays the temperature dependences of the growth rate and index of refraction for films deposited from HMDSO in argon atmosphere, GP 1, and GP 2. Quantitative deposition of oxide films begins at 500°C in GP 1 and only at 650°C in GP 2 and argon. The growth rate rises nearly exponentially in GP 1 and is almost linear with temperature in GP 2 and argon. The index of refraction of the films deposited in GP 2 increases with temperature, falling in the range 1.4–1.62. The *n* of the films grown in GP 1 is lower (1.25 to 1.5) and passes through a maximum around 550°C. The growth rate in GP 1 is higher by a factor of 4–10 than

in GP 2 and by a factor of 1.5-5 than in argon without  $N_2O$ .

The growth rate as a function of N<sub>2</sub>O flow rate at a constant HMDSO concentration ( $10^{-4}$  mol/l) shows a maximum at 2–2.5 mol/h, independent of temperature (Fig. 6). In the temperature range 500–650°C, the growth rate is substantially slower than that in the range 700–850°C. At lower temperatures, the highest deposition rate (3–14 nm/min) was observed in GP 1 at HMDSO : N<sub>2</sub>O molar ratios of 1 : 100 to 1 : 150. At higher temperatures, the deposition rate attains 36–60 nm/min at HMDSO : N<sub>2</sub>O from 1 : 150 to 1 : 200.

The Arrhenius plot of the deposition rate in GP 1 (Fig. 7) consists of two linear portions with a break at 750°C. The plots for CVD in GP 2 and argon are linear over the entire temperature range studied. For the CVD process in GP 1, the apparent activation energy  $E_a$  derived from the data in Fig. 7 is 84 kJ/mol in the range 500–750°C and 25 kJ/mol between 750 and 850°C. The  $E_a$  of CVD in GP 2 is 40 kJ/mol, and that of the process in argon without N<sub>2</sub>O is 54 kJ/mol. Thus, the introduction of N<sub>2</sub>O into the gas phase accelerates the deposition rate and changes  $E_a$ . The  $E_a$  of CVD in the pres-

ence of N<sub>2</sub>O is higher than that of the process without N<sub>2</sub>O by a factor of 1.6 in the temperature range 500-750°C and is lower by a factor of 2 between 750 and 850°C. The  $E_a$  of 25–40 kJ/mol indicates that both processes are diffusion-controlled [10]. The high  $E_a$  of the CVD process in GP 1 between 500 and 750°C testifies to an increase in the contribution of the reaction between HMDSO and N2O or products of its decomposition. In the range 750–850°C, the activation energy decreases abruptly, presumably because of the increasing effect of diffusion on the rate of the overall process. Two interrelated processes take place on the surface of the growing film: thermolysis and oxidation of the precursor. The variations in the activation energy and deposition rate seem to be due to different surface reactions between thermally activated HMDSO molecules and atmospheric oxygen or the atomic oxygen resulting from the decomposition of N<sub>2</sub>O or NO. As shown earlier [3, 4], during thermal nitridation of Si in the presence of N<sub>2</sub>O between 950 and 1000°C, N<sub>2</sub>O dissociates to form NO, oxygen, and nitrogen, and Si is oxidized by both NO and oxygen. The atomic oxygen appearing as a reaction intermediate affects the nitrogen content and distribution in the film. Clearly, in the CVD process in the presence of N<sub>2</sub>O, taking place at lower temperatures, the deposition rate between 750 and 850°C depends on the effects of both NO and O<sub>2</sub>. To assess the roles of NO and O<sub>2</sub>, we studied CVD from HMDSO in the presence of NO (GP 3) and NO + air (GP 4) at 650°C. As in the preceding experiments, the HMDSO concentration was maintained constant at 0.2  $\times$  $10^{-3}$  mol/l by adjusting the flow rate of argon carrier gas. The plots of deposition rate vs. NO flow rate (Fig. 8) show a maximum at an HMDSO : NO molar ratio of 1:50 in GP 3 and 1:57 in GP 4. At these molar ratios, the deposition rate in GP 4 (NO +  $O_2$ ) is almost twice as high (11.5 nm/min) as that in GP 3 (NO) (11.5 and 6.5 nm/min, respectively). In terms of the total amount of oxidants  $(NO + O_2)$ , the highest deposition rate in GP 4 was observed at an HMDSO :  $NO + O_2$ molar ratio of 1:87. At this molar ratio, the deposition rate in GP 3 (no oxygen) was 4-6 times slower. At HMDSO : NO = 1 : 87 in GP 3, the deposition rate was 2.7 nm/min (Fig. 8). Thus, the presence of air + NOmixtures (GP 4) or N<sub>2</sub>O (GP 1) ensures the highest deposition rates: 11.5 and 13 nm/min, respectively, at 650°C.

The AES depth profiles of the films deposited from HMDSO in different atmospheres are displayed in Fig. 9. CVD in GP 2 yielded films with the same combined Si : oxygen atomic ratio as in SiO<sub>2</sub> (Fig. 9a). The data for the films deposited in the presence of NO (GP 3) indicate a high content of free silicon near the film–substrate interface (Fig. 9b). The films deposited in GP 3 contain nitrogen and high concentrations of carbon as compared to GP 2. The observed combined Si : oxygen ratio indicates the formation of the unstable

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**Fig. 5.** (1, 2, 5) Deposition rate and (3, 4, 6) index of refraction vs. temperature for CVD from HMDSO in (1, 3) GP 1, (2, 4) GP 2, and (5, 6) N<sub>2</sub>O-free atmosphere;  $1.4 \times 10^{-2}$  mol/h HMDSO, 1.4 mol/h N<sub>2</sub>O, 1.4 mol/h air; HMDSO concentration in the gas phase,  $3 \times 10^{-4}$  mol/l.



**Fig. 6.** Deposition rate as a function of N<sub>2</sub>O flow rate at (1) 500, (2) 550, (3) 600, (4) 650, (5) 700, (6) 750, (7) 800, and (8) 850°C;  $1.2 \times 10^{-2}$  mol/h HMDSO, 2 l/h Ar; deposition time, 3 min.

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**Fig. 7.** Arrhenius plots of deposition rate for CVD in (1) GP 2, (2) argon without  $N_2O$ , and (3) GP 1.

monoxide SiO. Pyrolysis of oxygen-containing organosilicon compounds yields  $SiO_2$ , SiO, C, and organic radicals. The amount of SiO depends on the amount of reacting oxygen, which is supplied, for the most part,



**Fig. 8.** Deposition rate as a function of NO flow rate for CVD in (1) GP 3 and (2) GP 4.

by the organic molecule. The films deposited in GP 1 and GP 4 were found to differ markedly in composition from those deposited in GP2 and GP 3. As can be seen in Figs. 9c and 9d, the films deposited in GP 1 and GP 4



**Fig. 9.** AES depth profiles of oxide films deposited from HMDSO  $(1.4 \times 10^{-2} \text{ mol/h})$ : (a) GP 1 (0.7 mol/h N<sub>2</sub>O), 800°C; (b) GP 3 (0.7 mol/h NO), 650°C; (c) GP 2 (2.1 mol/h N<sub>2</sub>O), 800°C; (d) GP 4 (0.7 mol/h NO), 650°C.

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Table 4.	Electrical	properties	and growth	n rates of	f films de-
posited us	sing HMD	SO (1.4 mc	ol/h) at diffe	erent subs	strate tem-
peratures	and N <sub>2</sub> O:	HMDSO 1	ratios (GP 1	l, 2.1 mo	$l/h N_2O$ )

Substrate tempera- ture, °C	N <sub>2</sub> O : HMDSO molar ratio	v, nm/min	$\rho, \Omega  cm$	E <sub>br</sub> , V/cm
800	150	49	$6 \times 10^{13}$	$4 \times 10^{6}$
800	100	44	$7 \times 10^{8}$	$3 \times 10^{5}$
800	75	39	$4 \times 10^8$	$2.5 \times 10^5$
800	50	33	$6 \times 10^{8}$	$3 \times 10^{5}$
850	200	60	$4 \times 10^{13}$	$3 \times 10^{6}$

contain high levels of free Si distributed throughout the film thickness. The presence of free Si is likely due to the reaction  $2\text{SiO} \longrightarrow \text{SiO}_2 + \text{Si}$ , which is highly probable in GP 1 and GP 4 at high deposition rates. The absence and low content of free Si in the films grown in GP 3 and GP 2, respectively, are obviously due to the competing process  $\frac{1}{2}\text{Si} + x\text{O}_2 = \frac{1}{2}\text{SiO}_x$ . The films prepared in the presence of NO or N<sub>2</sub>O contained nitrogen at all depths. In the films grown in GP 4, carbon was present only in the top layer and its content was substantially lower in comparison with the films deposited in GP 1.

The IR spectra of the films deposited in the presence of N<sub>2</sub>O or NO contain bands at 1090 and 460 cm<sup>-1</sup> due to Si–O bonds and a broad band at 830–860 cm<sup>-1</sup> characteristic of the Si–N bonds in amorphous  $Si_3N_4$ films [11].

The electrical properties of the films were found to depend strongly on the gas-phase composition (Table 4). The highest resistivity and dielectric strength were found in the films grown in GP 1 at HMDSO :  $N_2O$  molar ratios of 1 : 150 (800°C) and 1 : 200 (850°C), corresponding to the highest deposition rate and stoichiometric combined Si: oxygen ratio. At other HMDSO : N<sub>2</sub>O ratios in GP 1, the breakdown strength  $E_{\rm br}$  and resistivity  $\rho$  were lower. Note that the advantageous dielectric properties of the films grown in GP 1 at 850°C and HMDSO :  $N_2O = 1 : 200$  may be due in certain measure to the formation of a thin buffer oxide layer [12]. The depth profile of the film deposited at 850°C demonstrates that only combined Si and oxygen are present at the film–substrate interface. The absence of carbon and nitrogen also suggests that a thin layer of oxidized Si is present at the interface. Clearly, the formation of this buffer layer accounts for the improved electrical properties of the films deposited from GP 2 and GP 4, containing air along with N<sub>2</sub>O and NO. The films deposited from GP 4 at HMDSO : NO :  $O_2 =$ 1:57 : 30 were close in resistivity and dielectric strength to the films grown in GP 1 at HMDSO :  $N_2O = 1$  : 150. The resistivity of the films deposited in the presence of only NO (GP 3) was one order of magnitude lower than that of the films grown in GP 1.

Electrical measurements on the  $Al_2O_3$  and  $SiO_2$ films deposited from aluminum acetylacetonate and HMDSO, respectively, in the presence of diethylamine show that this admixture has little effect on film properties. The most marked changes were found in dielectric permittivity, which was higher by a factor of 1.5–2 in the films grown in the presence of diethylamine in comparison with those produced in air, which is attributable to the higher carbon content of the latter.

#### CONCLUSION

Our results on the CVD of SiO<sub>2</sub> films on Si via pyrolysis of HMDSO in the presence of  $N_2O$ , NO, or NO + air mixtures demonstrate that the deposition rate and film composition depend on the gas-phase composition and HMDSO : oxidant molar ratio. The effects of  $N_2O$  (GP 1) and NO + air mixtures (GP 4) on the deposition rate and film composition are somewhat similar, in accordance with the fact that these atmospheres are close in composition at high temperatures because of the  $N_2O$  decomposition into NO and oxygen. At low temperatures, the CVD process is limited mainly by the rate of surface reactions, which is in turn controlled by the rate of chemisorption. At high temperatures, the process is limited by the rate of reactant transport, which is a weak function of temperature. The increase in deposition rate as the temperature is raised from 500-750 to 750-850°C and the decrease in the HMDSO :  $N_2O$  ratio ensuring the highest growth rate suggest that the CVD process is limited by the thermolysis of the metalorganic precursor. The same is evidenced by the AES depth profiling data.

The introduction of diethylamine into the gas phase has a significant effect on the deposition kinetics, increasing (in the case of aluminum acetylacetonate) or reducing (in the case of HMDSO) the growth rate. This effect depends strongly on whether the reaction takes place on the substrates surface or in the gas phase. The growth kinetics, composition, and properties of the films depends on the extent of decomposition—to an oxide or to an intermediate complex of diethylamine (or products of its decomposition) with aluminum acetylacetonate or HMDSO.

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