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REVIEW

CHEMICAL VAPOR DEPOSITION OF ALUMINUM FOR ULSI APPLICATIONS

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Abstract – Aluminum has been used widely as a conducting material in the fabrication of integrated circuits, and chemical vapor deposition process for Al has been actively investigated for the application in ultra large scale integration. In this review, various precursors, mainly alkyl aluminum and alane compounds, and reaction mechanisms of these precursors in Al CVD are described. Epitaxial growth and selectivity of the deposition are also discussed. In addition to thermal reactions, plasma and photochemical reactions are also briefly described.

Key words: *Chemical Vapor Deposition (CVD) of Aluminum, Aluminum Thin Film, Selective Deposition, Metal Organic CVD*

INTRODUCTION

Al thin films are widely used in many industrial applications such as metallized polymers for packaging, optical coatings for mirrors and compact discs, and interconnects in microelectronic devices [1-9]. Metallized polymers are used as a diffusion barrier for water, oxygen and other gases. For this applications, films should be pinhole free and specularly reflective to visible light for good appearance. The reflectivity of Al is second only to Ag and information storage on compact discs utilizes the reflectivity of Al films on polycarbonate. Specularly reflective films require smooth surfaces and most mirror like Al films are composed of a large number of grains less than 200 nm in diameter. Tinted glass utilizes the absorptivity of very thin (10 nm) Al films to reduce the amount of light, especially in the infrared region, transmitted through a window.

The resistivity of bulk Al is 2.74 μΩ-cm, which is only slightly greater than that of Ag (1.61 μΩ-cm) and copper (1.70 μΩ-cm). Low resistivity is desirable as an interconnect material because device speed can be faster. Al films also adhere well to Si, SiO_2, other metals, and some polymers. Al can be easily etched despite a native oxide formation, which is also important in the patterning of micro circuits. Al has been used widely in the metallization of integrated circuits because of these advantages even though there has been a concern [10] about its susceptibility towards electromigration, large discrepancy in thermal expansion coefficient with silicon, and reactivity with semiconductors.

So far, most of commercial Al films have been deposited by physical vapor deposition, *i.e.*, sputtering and evaporation [11-16]. They can produce films of high purity and deposition temperature can be as low as room temperature. Al films deposited by PVD are mainly polycrystalline and models relating growth conditions to the micro structure have been described [17-23]. High vacuum conditions are needed for PVD process but most CVD processes are operated in the range of low (about 0.1 torr) to atmospheric pressure. With PVD process, it is difficult to deposit films with good conformality on submicron feature sizes because it gives mainly line of sight deposition due to the large values of mean free path and the high sticking coefficient of metal atoms or clusters. In CVD, the mean free path of the molecules and their sticking coefficients are smaller and also the molecules or fragments have more time to migrate on the surface before they form a solid deposit through chemical reactions. Because of this, CVD processing usually gives more conformal coverage of a surface [5, 24] and allows a reactor design for multiwafer processing to give high throughput. For this reason, Al CVD [25-28] has been actively investigated for ULSI applications like 256 mega or 1 giga bit DRAM fabrication.

CVD process has some disadvantages, *i.e.*, difficulty in handling chemicals, maintaining a pure and safe system, and high cost of the molecular precursors. Some contaminants are present in the source of the precursors and also precursors can undergo unwanted side reactions causing impurity incorporation in the film. Depositions of thin films with CVD usually require substrate temperatures higher than PVD. The relative complexity of CVD requires a greater effort to develop a sucessful process and understanding of precursor chemistry is essential to design an optimized CVD system for high quality thin films.

In this review, various precursors, mainly alkyl aluminum and alane compounds, and their reaction mechanisms in the gas phase and on the substrate surface in Al CVD are described. Epitaxial growth and selectivity of the deposition are also discussed. In addition to thermal reactions, plasma and photochemical reactions are also briefly described. Other aspects of CVD such as fluid mechanics and transport phenomena, which is also important in the design of a CVD reactor, has been described elsewhere [29-34].

PRECURSOR CHEMISTRY

Table 1 summarizes some of the precursors widely investigated for Al CVD and their properties [35, 36]. CVD precursor should have appreciable vapor pressure to be transported into the reactor without condensation. It should also be stable enough so that it does not dissociate to form a solid phase before it reaches the substrate surface. On the substrate surface, it should dissociate

Table 1. Al CVD precursors and their characteristics

Precursor	Vapor pressure torr (℃)	Growth temp.* ℃	Selectivity**
Trimethylaluminum (TMA)	11 (20)	300	none
Triethylaluminum (TEA)	0.1 (36)	160	-
Triisobutylaluminum (TIBA)	0.1 (27)	250	Si
Dimethylaluminum hydride (DMAH)	2 (25)	230	Si
Diethylaluminum chloride (DEACl)	3 (60)	340	Si
Trimethylamine alane (TMAA)	1.1 (19)	100	Metals
Triethylamine alane (TEAA)	0.5 (25)	100	-
Dimethylethylamine alane (DMEAA)	1.5 (25)	100	Metals
Trimethylamine aluminoborane (TMAAB)	-	100	-

*approximate lowest temperature reported for a thermal deposition.
**preference for thermal growth on the material in the presence of SiO_2.

effectively to form a deposit without the incorporation of impurity atoms from the precursor molecules and reaction byproducts.

Some of the precursors which have received the most attention to date and their chemistry involved in the deposition process will be described below.

1. Alkylaluminum

1-1. Triisobutylaluminum (TIBA)

TIBA has received the most attention for Al CVD and since early 1980s, several groups demonstrated the usefulness of this precursor for integrated circuit applications [37-39]. A hot wall reactor at 200-300℃ and 0.2-0.5 torr was used with deposition rate around 20-80 nm/min. TIBA is a colorless and pyrophoric liquid having a vapor pressure of about 0.1 Torr at ambient temperature. It is known to be monomeric in the vapor phase and its structure is given in Fig. 1(A). It has been used as a catalyst for the polymerization of olefins and was found to produce high quality Al thin films with purity higher than 99 atom% through CVD [40]. The mechanism to liberate the isobutyl groups is the well-known β-hydrogen elimination reaction as shown in Fig. 2(A).

At temperatures above 50℃, TIBA loses one isobutyl ligand and forms diisobutylaluminum hydride (DIBAH). It has a substantially lower vapor pressure (0.01 torr at 40℃) because it exists as a hydrogen bridged trimer as shown in Fig. 1(B). When the precursor vessel and the gas lines are heated to 40-50℃ to prevent the condensation of TIBA, the formation of some DIBAH is likely. Its formation has caused a reduction in the reflectivity of Al films (increase in surface roughness) [41]. The addition of excess isobutene to the carrier gas can suppress the dissociation [40]. Above approximately 200℃, DIBAH reacts to give Al and most CVD studies employ a temperature higher than this in order to obtain useful deposition rates. Aluminum can also be deposited directly from TIBA without DIBAH formation [42-45]. TIBA also reacts with sources of oxygen to form alkoxides as shown in Eq. (1). These alkoxides can be volatile and can therefore be a source of contamination in the film [46, 47]. The problem has been avoided with the use of a distillation system located upstream of the reaction zone [41].

$$Al(i\text{-}Bu)_3 + (3-x)/2\ O_2 \rightarrow Al(O\text{-}i\text{-}Bu)_{3-x}(i\text{-}Bu)_x\quad (x=0-2) \qquad (1)$$

The surface chemistry of TIBA pyrolysis was investigated with effusive molecular beam scattering, TDS (thermal desorption spectroscopy), AES, low energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), and SEM in a UHV system [42-45]. The decomposition of TIBA on Al(100) and Al(111) surfaces took place at about 200℃ to form carbon-free epitaxial Al, H_2 and isobutene [44]. Both hydrogen and isobutene readily desorb from Al surface below the decomposition temperature indicating that product desorption is not rate limiting. The rate of formation of isobutene was first order with respect to the flux of TIBA. Following TIBA adsorption, each of the isobutyl groups then participates in a rate determining β-hydrogen elimination reaction to liberate isobutene and form a surface bound hydrogen atom [48-51]. Molecular TIBA desorption was never observed in the TDS study. The rate of the surface process is 2-5 times faster on Al(111) than on Al(100), which is presumably due to the respective work functions of Al(111) and Al(100). Above 330℃ and 350℃ for Al(100) and Al(111) surfaces, respectively, carbon incorporation was evident from a more highly activated β-methyl elimination step of an isobutyl ligand as shown in Fig. 2(B).

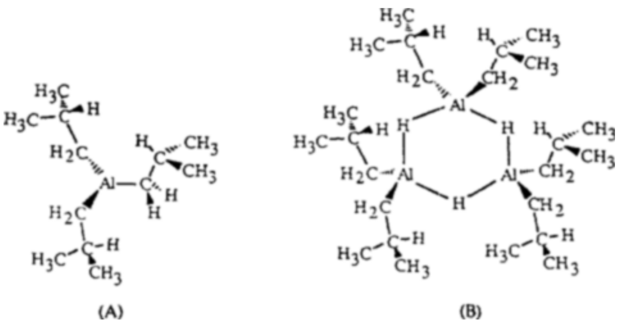


Fig. 1. Structure of (A) triisobutylaluminum and (B) diisobutylaluminum hydride trimer.

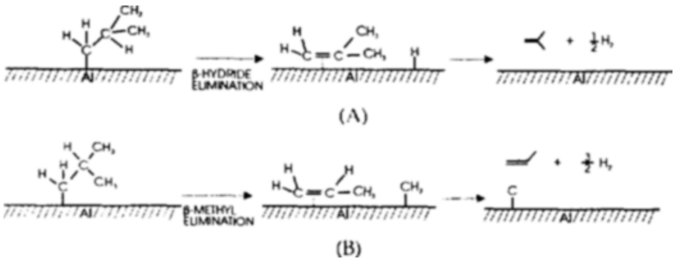


Fig. 2. Surface reaction mechanism of Al CVD from triisobutylaluminum (A) β-hydride elimination reaction below 600°K and (B) β-methyl elimination reaction at higher temperatures.

The reluctance of TIBA to deposit Al onto SiO_2 has been used to grow selectively on silicon and Al surfaces [38]. The selectivity in such depositions is established at the nucleation stage of film growth. The mechanism behind selective area growth was investigated in a series of X-ray photo emission spectroscopy (XPS) studies in a UHV environment [52-54]. The reason for the difference in the growth rates on the different surfaces was traced to the interaction of TIBA with oxygen in SiO_2. Upon adsorption of TIBA on SiO_2, the first two isobutyl groups were readily released, even at room temperature [52]. The β-hydride elimination for the third isobutyl group, however, was suppressed, and the monoisobutylaluminum species inhibited film growth on SiO_2 by preventing further adsorption of TIBA [53, 54]. No decomposition of this last isobutyl group was observed even when the surface of the substrate was maintained above typical growth temperatures (450℃).

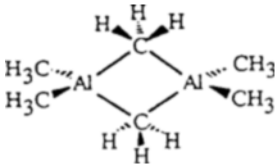


Fig. 3. Trimethylaluminum in dimeric form.

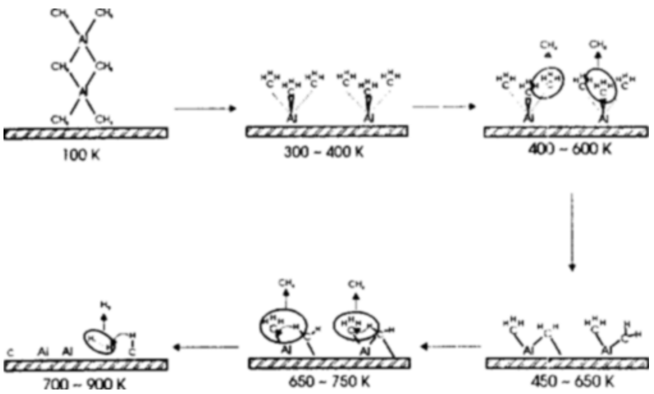


Fig. 4. TMA surface decomposition mechanism on Si(100).

It was suggested that the activation energy for β-hydride elimination reaction became higher when Al is bound to an electronegative atom such as oxygen [55, 56]. This may explain the reluctance of the last isobutyl group in TIBA to be removed from SiO_2 surface. Native oxides of Al surface also inhibits the nucleation.

1-2. Trimethylaluminum (TMA)

This precursor is a liquid at room temperature with a vapor pressure of about 11 torr at 20℃. It exists as a dimer in the gas phase at ambient temperatures and as a monomer at elevated temperatures (~200℃) [57]. The structure of the dimer given in Fig. 3 shows that it contains both terminal and bridging methyl groups bound to Al [58]. TMA has been shown to adsorb on the surface of silicon substrates up to ambient temperatures as a dimer with the long axis of the molecule perpendicular to the substrate surface [59-62].

Deposition temperature for TMA is in the range of 350-550℃ [63]. The mechanism for the decomposition of TMA both in the gas phase and on the surface is complex, and a number of studies have shown that the path is strongly dependent on the reaction conditions and substrate surfaces. There is no general agreement on the mechanism of aluminum deposition from TMA and it is complicated by competing reactions which lead to the incorporation of relatively high amount of carbon into the film. Both the liberation of reactive radical species such as CH_3 [64, 65] and stable molecular species such as CH_4 [62, 66-70] have been proposed as mechanisms of TMA decomposition. TDS, XPS, and EELS analysis showed that monomeric TMA on the surface of a Si(100) substrate was fragmented by an intramolecular pathway to eject CH_4 [62, 66, 68] as shown in Fig. 4. Carbon incorporation was attributed to the decomposition reaction on the substrate surface to produce elemental carbon or C-H. Small amount of CH_4 was shown to be evolved from a clean, polycrystalline Al surface following exposure to TMA [69, 70] and in this case, large quantities of C remained on the surface. In contrast, methyl radicals were detected by mass spectrometry when a beam of TMA was reacted with a variety of surfaces (Cu, Al, quartz and GaAs) at temperatures in the range of 280-630℃ [64, 65].

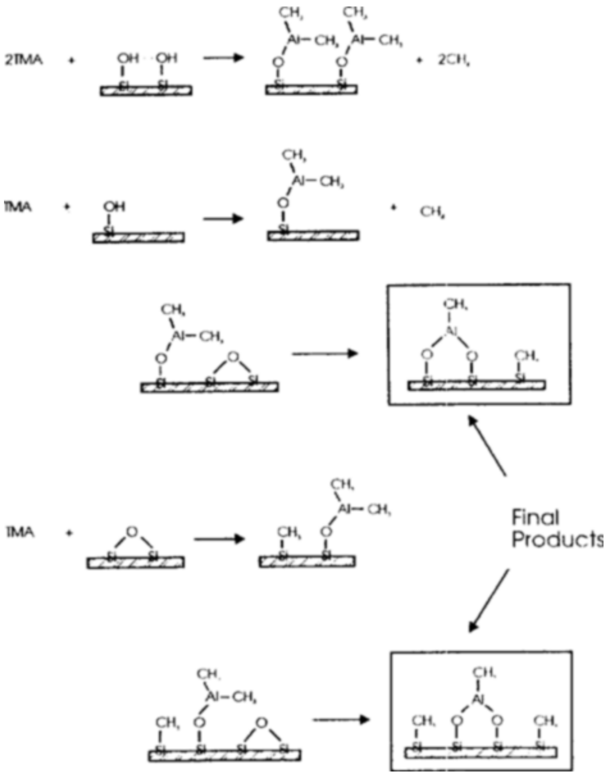


Fig. 5. Reaction mechanism of trimethylaluminum on SiO_2 surface.

A number of researchers have investigated the mechanism for TMA chemisorption on SiO_2 and Al_2O_3 and have found carbon to be a byproduct of the decomposition [71]. A summary of the proposed reactions is outlined in Fig. 5. In the case of TMA adsorption on Ru(001), the dominant desorption product was H_2 [72].

It was shown that aluminum films deposited by the pyrolytic decomposition of TMA contained high levels of carbon in the bulk of the film as well as at the substrate surface [73-76] with stoichiometry approaching Al_4C_3. The formation of Al_4C_3 thin films is consistent with the assumed product from the thermal decomposition of TMA [77]. FT-IR spectroscopy was used to quantitate the decomposition of TMA in a sealed stainless steel reactor heated to 150℃ and established that the reaction was first order in TMA and that the overall stoichiometry was

$$Al_2(CH_3)_6 \rightarrow 1/2Al_4C_3 + 9/2CH_4 \text{ (under } N_2). \quad (2)$$

Changing the atmosphere from N_2 to H_2 did not change the activation energy for the decomposition, although it did result in the formation of aluminum as

$$Al_2(CH_3)_6 + 3H_2 \rightarrow 2Al + 6CH_4 \text{ (under } H_2). \quad (3)$$

In a pyrex cylinder, at significantly higher TMA pressures (9.1-85.5 torr) and temperatures (298-334℃), the reaction products consisted largely of CH_4 and lesser amounts of ethane, ethylene and H_2 [73]. Thermodynamic calculations on the thermal decomposition of TMA were used to predict the nature and relative amounts of equilibrium products [78].

In summary, TMA is of questionable value for CVD applications due to the tendency for carbon to be incorporated into the film.

1-3. Other alkylaluminum

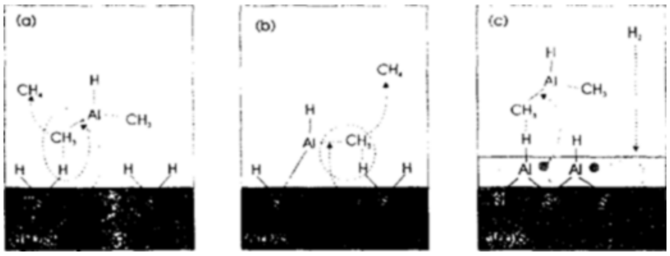


Fig. 6. A surface electrochemical reaction model for the selective growth of Al from DMAH.

Other alkylaluminum sources such as TEA, DMAH and DEACl have been investigated to a lesser degree than two precursors already discussed. They are also pyrophoric and react vigorously with moisture. Additionally, they tend to exist in an associated state in the gas phase, particularly in the form of dimers.

Triethylaluminum (TEA) is a liquid at room temperature and has a vapor pressure of 0.1 torr at 36℃. The low vapor pressure requires the precursor to be heated higher than 40℃ [79]. The kinetics of the thermal decomposition of gaseous TEA were reported using a closed system in the temperature range of 160-190℃ and a pressure of approximately 50 torr [80]. An independent study showed that films of Al deposited from gaseous TEA contain Al carbide as well as elemental carbon with the concentration increasing with temperature. Lower carbon incorporation is evident, however, relative to TMA [81, 82]. This fact probably reflects the importance of the β-hydride elimination and is a notable example of how the composition and the micro structure of a film depend on the structure of the molecular precursor.

Dimethylaluminum hydride (DMAH) is a liquid at room temperature with a vapor pressure of 2 torr at 25℃ [83]. The pure liquid state has a degree of association of at least three. In the vapor, it is trimeric at low temperatures and becomes dimeric at around 160℃. Unlike TMA and TEA which are alkyl bridged structures, the Al atoms in DMAH are bridged by hydrogen [84]. The heat of association of 15-20 kcal/mol per H bridge is typically higher than that for the CH_3 bridges in TMA having a value of about 10 kcal/mol per CH_3 [85]. DMAH pyrolysis has been performed at temperatures from 230-280℃ in a hydrogen gas flow of a few torr [79, 86, 87]. Selective growth of Al on Si in the presence of SiO_2 using DMAH has been observed [86, 87]. In one study, an optimized temperature range of 235-245℃ was used [87]. At 200℃, no deposit was found on either the Si or SiO_2 according to optical micrographs, while at 310℃, Al was deposited on both Si and SiO_2 with islands of Al appearing on the oxide surface. In a related report, a temperature of 270℃ was used for selective growth [86]. As a generalization, selectivity was possible on electrically conducting substrates like TiN and doped silicon but not on insulating materials such as SiO_2 and borophosphosilicate glass. This precursor is believed to give good Al film with low carbon contamination and good selectivity and has been widely used by Japanese researchers. A surface electrochemical reaction model, where surface free electrons catalytically contribute to the reaction, for selective growth of Al from DMAH is shown in Fig. 6.

Diethylaluminum chloride (DEACl) is also a liquid at ambient temperature and aluminum films have been grown from DEACl at 310-380℃ in a cold wall system with a stream of hydrogen carrier gas [88]. In the presence of Si(100) and SiO_2, the Al deposits were confined to the silicon surface. The precursor required heating to 60℃ in order to obtain a convenient vapor pressure. A film deposited on polycrystalline silicon at 340℃ was grown at a rate faster than 37 nm/min and had a resistivity of 5.1 μΩ-cm. Despite the faster deposition rates encountered on Si(111), the activation energy on both Si(111) and Si(100) surfaces was 39 kcal/mol. A pathway where AlCl was reduced by surface silicon was suggested [89].

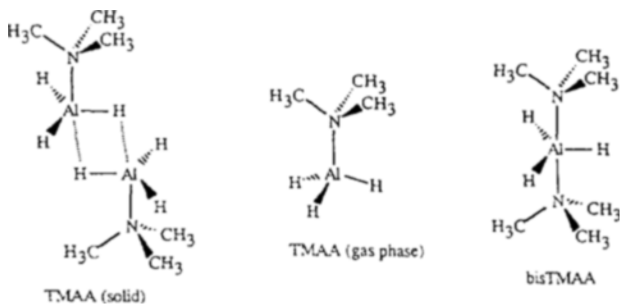


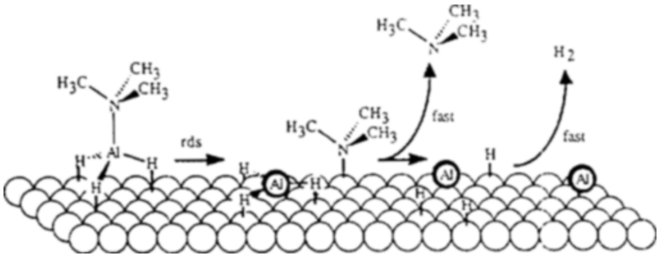
Fig. 7. Molecular structure of trimethylamine alane in dimeric form in the solid phase, monomeric form in the gas phase, and bis adducts.

2. Alane Compounds

Alane (aluminum hydride, AlH_3) itself is an unstable vapor at ambient temperatures which polymerizes to form a low vapor pressure, solid containing bridging Al hydrogen bonds of the type Al-H-Al [36]. The coordination of the Lewis acid, AlH_3, with a Lewis base, which donates a single pair of valence electrons to the metal, gives rise to a relatively stable donor-acceptor complex. In this structure, the Al atom possesses an octet of valence electrons which makes it stable against polymerization. The commonly known basic donors are amines such as Me_3N, Me_2EtN and Et_3N. These precursors are readily synthesized from one step reactions involving $LiAlH_4$ and the hydrochloride salt of amine [90]. Trimethylamine alane (TMAA) [91-94], triethylamine alane (TEAA) [95-97], dimethylethylamine alane (DMEAA) [98, 99] and $(Me_3N)AlH_2(BH_4)$ [100] adducts have been the focus to grow Al films. These adducts of alane do not contain Al-C bonds, and the Al-N bond is easily cleaved. As a result, problems of carbon incorporation are minimized. In one study, carbon incorporation was below the background of Secondary Ion Mass Spectrometry (SIMS) (2×10^{18} atoms/cc or 10^{-3}%) [101] and the level of carbon was similar to that found in a device quality sputter deposited Al film [102]. As a result of the promise shown by these compounds in the field of Al and Al related CVD processes (AlGaAs), they have begun to appear on the commercial market.

2-1. Trimethylamine alane (TMAA)

Several groups showed the potential of the precursor molecule $(Me_3N)AlH_3$ (TMAA) for CVD applications [91-94]. Pure aluminum films were deposited from this solid precursor at relatively high deposition rates and at temperatures below 100℃. With trimethylamine, both the mono and the bis adducts are known and their structures are shown in Fig. 7. These two adducts exist in a gas phase in equilibrium with the crystalline phase of the 2 : 1 complex [103]. The 1 : 1 adducts is a monomer in the gas phase [104, 105] but in the condensed state, it exists as a dimer [106]. The 2 : 1 adduct, on the other hand, is a monomer in both the condensed [107] and gaseous phases [104]. Both the 1 : 1 and the 2 : 1 adducts of TMAA are colorless crystalline solids having vapor pressures of about 1 and 2 torr at 25℃, respectively.



Although these precursors display sensitivity to atmospheric H_2O and O_2, they are significantly less air sensitive than the alkyl Al compounds and are not pyrophoric unless exposed to high humidity conditions. In the atmosphere, the complexes decompose to give involatile Al oxides and hydroxides. This means that the inevitable decomposition of the precursor due to the presence of residual contaminants results in byproducts which are not readily transported to the deposition zone and therefore do not contribute to the contamination in the film.

Studies have shown that the pyrolysis of TMAA produces Al films at temperatures below 100℃ and liberates molecular hydrogen along with trimethylamine. The adsorption and kinetics of film growth from TMAA has been investigated [108] and it was decomposed on Al(111), Al(100) and Si(111) single crystal surfaces as well as on Al_2O_3 [108-110]. A distinction in the behavior of the decomposition on Al surfaces at temperatures below and above ambient was made. For Al(111) and Al(100) substrate with temperatures in the range of −190 to 10℃, the reactive sticking probabilities were low (<0.01) with molecular desorption dominating in the TDS studies. Small amount of decomposition that were noticed was attributed to surface defect sites. Using molecular beam scattering, it was established that above 30℃, growth of epitaxial Al took place with increasingly high efficiency (greater or equal to 0.5 at 30℃) suggesting that a majority of the Al(100) and Al(111) sites were involved. Trimethylamine and H_2 were the observed desorption products. The Al films were highly reflective even for thicknesses above 1000 nm and no C, N or O were detected either in the bulk or on the surface of the film by AES.

On the basis of the surface studies [111-114], a decomposition pathway was proposed for the surface reaction under steady growth conditions as shown in Fig. 8. With TIBA, the ability to disperse the alkyl ligands over an Al surface facilitated the deposition. A similar scheme has been proposed for TMAA with the hydrogen atoms dispersing themselves over the Al surface. This behavior of hydrogen is reflected in the TDS data for H_2 desorption from single crystal Al where a single H_2 desorption peak is observed at temperatures near 30℃. Film growth on Al_2O_3 and Si(111) surfaces proved to be more difficult. Nucleation on Si was more highly activated than the steady state growth on Al giving rise to the formation of polycrystalline Al, textured in the (111) direction.

Depositions using TMMA in a cold wall reactor took place in the temperature range of 200 to 350℃ and resulted in growth rates of up to 140 nm/min at TMAA pressures of 75 mtorr. Although typical depositions were carried out at 250℃, growth on Cu substrates was possible at temperatures down to 85℃ and higher growth rates (in excess of 1000 nm/min) have been observed below 200℃ [101]. Depositions conducted in hot-wall reactors are more likely to have a contribution from gas phase chemistry. For example, the dissociation of one of the trimethylamine ligands from $(Me_3N)_2AlH_3$ occurs in the gas phase at room temperature [115] as

$$(Me_3N)_2AlH_3 \rightarrow (Me_3N)AlH_3 + Me_3N. \qquad (4)$$

As the deposition of Al proceeds, the steady state concentration of Me_3N will affect the equilibrium of above reaction. Because of the high reactivity of AlH_3, even the formation of very small quantities could be important, especially in the nucleation stage of film formation or in the formation of particles in the gas phase.

The so-called incubation period that is encountered before Al growth is observed on Si and SiO_2 substrates from alane and this has been used to grow Al films selectively on metallic surfaces [99, 101]. Aluminum has been deposited selectively on metals such as Au, Cu, and W in the presence of Si. Once the critical nucleus size [116-119] is formed, steady state growth will continue regardless of the original substrate. Number of factors could affect the formation of the critical nucleus. For example, a small sticking coefficient of the precursor on one of the surfaces could diminish the probability of supersaturation necessary to induce the nucleation. It is also possible that a surface sensitive chemical reaction must take place to generate the growth species. As mentioned above, a large activation barrier exists for hydrogen elimination from isolated alane molecules. The selectivity of growth on metallic surfaces may be the result of their ability to catalyze the desorption of hydrogen. On surfaces such as SiO_2, hydrogen desorption may be slow unless an Al cluster has formed allowing the growth to sustain itself. In support of this, it has already been mentioned that Al nucleation on Si and GaAs surfaces is slower than on Al. Both of these surfaces desorb H_2 at significantly higher temperatures than Al [109, 110, 120].

Aluminum films have been selectively deposited from TMAA onto SiO_2 without heating the substrate using laser assisted chemical vapor deposition and focused ion beam stimulated deposition techniques [92, 94, 121].

2-2. Triethylamine alane (TEAA) and dimethylethylamine alane (DMEAA)

TEAA is a clear colorless liquid with vapor pressures of 1.5 torr at 25℃ and it does not appear to exist as the bis adduct. Liquid precursors are desirable because they provide a constant, more easily reproducible flux of precursor into the reactor compared to solid precursors. Al films grown from TEAA had low impurity levels according to SIMS [95]. Its lower vapor pressure resulted in slower growth rates (still 2-4 times those of TIBA at 250℃) although the film morphologies were similar at comparable temperatures and pressures. The surface decomposition pathway in a UHV environment has also been studied [97] and the structural similarity of TMAA and TEAA suggested that the overall decomposition mechanism for TEAA should be similar to that for TMAA.

Despite the similarities in the decomposition of TMAA and TEAA, there was also a striking difference in the kinetics which has been related to the difference in the Al-N bond energy in changing the donor ligand from trimethylamine to the more sterically incumbering triethylamine. TDS experiments with TEAA demonstrated that H_2 was the species which desorbed from the surface at the highest temperature and H_2 desorption was suggested as the rate limiting step in the surface kinetics [97]. The kinetics of decomposition on the surface for TMAA and TEAA are controlled by the rate of Al-N bond cleavage and the rate of H_2 desorption, respectively.

DMEAA was isolated as the 1 : 1 adduct but the mass spectral evidence suggests that a small, but detectable, amount of the bis adduct is present [99]. It is the most recently introduced member of the amine family of precursors. Its relatively high vapor pressure at room temperature (1.5 torr), its long shelf life, combined with the advantages of being a liquid have made it the precursor of attention recently [98, 99]. At 170℃, the growth rate in a hot-wall reactor at a precursor partial pressure of 0.3 torr (total pressure with $H_2=3.3$ torr) on Cu substrates was 150 nm/min. The films were polycrystalline containing no detectable impurities as measured by AES. Detailed kinetic study has not been reported yet.

EPITAXY

Epitaxial Al film draws much attention because of its stronger electromigration resistance. With great care, epitaxial films of Al have been grown on the surface of Si(100) and Si(111) substrates using a technique referred to as gas-temperature-controlled CVD (GTC-CVD) [122-126]. In this technique, the precursor is preheated before its arrival at a heated substrate surface. It was proposed that reactive gas phase intermediates were formed and impinged on the substrate to promote the decomposition to Al. TIBA was introduced into the reaction zone by bubbling argon into a cylinder at 50℃. The gases, at a total pressure of 2 torr, were then preheated to 230℃ in a copper cylinder. Upon exiting the cylinder, they came in contact with a silicon substrate. With a substrate temperature of 400℃, smooth epitaxial films of Al(111) were grown on Si(111) as evidenced by reflective high energy electron diffraction (RHEED). The typical growth rate at 400℃ was about 900 nm/min. Such films were highly reflective (>90% specular between 310 to 600 nm) and had resistivities close to the bulk Al. Apart from the diffusion of 0.1% Si into the film, low levels of O, C and H were detected (~20 ppm). An Arrhenius plot of the growth rate on Si(111) below 300℃ gave an activation energy of 30 kcal/mol for the surface reaction. Film growth was monitored with scanning electron microscopy (SEM) which indicated that Al islands with a low nucleation density grew initially on the silicon surface and coalesced at a film thickness of about 300 nm. Small changes in the temperature of the substrate had a dramatic effect on the film morphology so that below 400℃, the Al surface became rough and contained a mixture of the (111) and (100) orientations. Further work using transmission electron diffraction (TED) established that epitaxial Al(100) was formed on Si(100) at 380-400℃ using this deposition procedure. Near 400℃, the surface became rough again and the films were a mixed structure of Al(100) and (110). At higher temperatures, films were (110) oriented although the grains were rotated 90° to each other. At temperatures below 380℃, the surface was rough and the films were polycrystalline.

The temperature sensitivity of Al growth on Si(111) has been studied independently using a set-up similar to that used in the above two studies although the gases were not preheated prior to their arrival at the growth surface [127]. With transmission electron diffraction (TED), epitaxial Al(100)//Si(111) with Al[110]/Si[112] was observed at 380℃ whereas at around 420℃, a much smoother single crystal of Al(111)//Si(111) with Al[110]//Si[110] was grown. Films grown at 400℃ were polycrystalline with intermediate reflectivity and resistivity. The epitaxial relation appeared to be determined mainly at the initial stage of growth and was probably related to the interfacial energies between Al and Si at different temperatures rather than to a change in CVD mechanism. Cross-sectional micrographs of the interface between Al and Si showed that the films deposited at 420℃ were comparatively dislocation free.

The ability to grow epitaxial films of Al on Si is curious considering the lattice mismatch of 25%. Epitaxial films have also been grown by physical vapor deposition techniques, however. The mismatch can be accomodated if one assumes a small displacement between Al and Si lattices at the interface over multiple unit cells. Atomically resolved transmission electron micrographs (TEM) were used to investigate the lattice matching at the Al(111)//Si(111) interface and four lattice planes of Al appeared to occupy the same distance as three lattice planes of Si [128].

NUCLEATION PROMOTERS

Aluminum deposition did not take place readily on the surface of silicon substrates unless the surfaces had been pretreated with TIBA at a temperature significantly above the typical decomposition temperature. It has been observed that the decomposition on the surface of silicon is a more highly activated process. Al island nucleation on silicon is favored over silicon oxide surfaces and Al films on silicon substrates typically exhibit better uniformity of coverage [39]. Nucleation promoters have been used to initiate film growth and to enhance the uniformity and smoothness of deposits. For example, when silicon substrates are exposed in situ to $TiCl_4$ prior to Al deposition (the excess vapors being pumped out of the system before the reactor is exposed to TIBA) dramatic differences in Al film uniformity are observed [37, 41].

The mechanism of nucleation promotion by $TiCl_4$ is not clearly understood yet. The saturation coverage of Ti on SiO_2 substrates is consistent with a surface OH coverage of about 15-30% of a monolayer and it has therefore been suggested that the incorporation of Ti onto SiO_2 occurs via a hydrolysis reaction between $TiCl_4$ and the surface hydroxyl groups [129-132] as

$$(\text{-O})_3\text{Si-OH} + \text{TiCl}_4 \rightarrow \text{HCl} + (\text{-O})_3\text{Si-O-TiCl}_3. \tag{5}$$

TDS studies in which SiO_2 was treated with $TiCl_4$ produced two desorption peaks occurring at −90℃ and +90℃. The low temperature signal was attributed to the desorption of $TiCl_4$ multilayers, whereas the higher temperature peak resulted from desorption of the $TiCl_4$ bound to the substrate. Parallel studies of the surface composition using AES showed that only half of the $TiCl_4$ desorbed at 90℃. Above this temperature, the Cl/Ti ratio slowly dropped until by 600℃ no Cl signal was visible. This change was attributed to the slow loss of HCl from the surface. Qualitative experiments suggested that any $TiCl_4$ present on the surface would promote nucleation.

A variety of metal catalysts have been shown to promote the decomposition of metal alkyls [133]. These catalysts include $TiCl_4$, TiH_2, $CrCl_3$, VCl_4, and $NbCl_5$. Not only they hasten the decomposition reaction, but they also reduce the temperature of the decomposition. Seed layers of TiN, Cu, Au, Ni [134], and Cr [37, 38] can also be beneficial to film nucleation and growth. In a hot wall reactor at 230-270℃ under typical low pressure conditions, films grown on SiO_2 coated in situ with sputtered TiN were smooth, highly reflective, conducting and relatively free from pinholes, interfacial voids and stress. Other advancements have been made to increase the smoothness of deposits. Preheating the gases before their arrival at the substrate surface [122] and the introduction of O_2 in low concentration [40] during a deposition have met with some success.

Nucleation difficulties, similar to those with TIBA, have been encountered during the growth of Al films from TMAA on the surface of Si and SiO_2. The same idea has been used with TMAA initially in hot-wall reactors [91, 93] and more recently in cold-wall systems [96, 101, 102]. Once again, not only has this resulted in more uniform nucleation, it has also reduced the temperature at which Al can be grown. For example, Al films have been successfully grown on TiN, Cu, and $TiCl_4$-treated Si and SiO_2 [96, 102]. Highly oriented polycrystalline (111) films were grown on $TiCl_4$-treated SiO_2 and TiN. On both $TiCl_4$-treated Si(100) and on Cu, the films were randomly oriented, although the latter films did favor growth in the (100) direction. Films with a thickness up to 200-300 nm were highly reflective but at greater thicknesses, the films showed a white haze which was attributed to an increase in surface roughness. Both grain size and crystal faceting increased with deposition temperature for all surfaces. Little is known about the reaction between TMAA and $TiCl_4$.

PLASMA AND PHOTO CVD

1. Plasma CVD

A radio frequency plasma chemical reactions of TMA in the gas phase formed $Al(CH_3)_2$ and $Al(CH_3)$ [135]. These subsequently decomposed at the substrate surface (230-260°C) to give Al films which were free from carbon according to XPS analysis. Deposition rates of up to 30 nm/min were achieved. The as-deposited films were strongly (100) oriented, reflective and hac resistivities as low as 2.7 μΩ-cm. An additional freature of interest was the ability to deposit the Al films selectively on a silicon surface in the presence of SiO_2. A critical factor was the need for a low plasma power. Higher power caused TMA to decompose into more fragmented species and resulted in carbon incorporation [136]. Films deposited using TMA and H_2 mixture and a silicon substrate temperature below 100°C had resistivities of about 3.8 μΩ-cm and a carbon content of around 6%. In contrast to other studies, films deposited in this manner were smooth.

Non-selective deposits from dimethylaluminum hydride (DMAH) could be obtained with the use of a radio frequency generated plasma above the sample surface [86]. The plasma was used for one minute and was found to induce nucleation on SiO_2. Once growth had been initiated, subsequent deposition took place on the prenucleated Al in the absence of the plasma.

2. Photo CVD

Ultraviolet (UV) laser irradiation of a substrate surface [137] in the presence of an Al alkyl precursor such as TIBA has been shown to have a beneficial effect on the growth of Al films. The principle behind this technique is to prenucleate a substrate surface with laser deposited Al so that subsequent thermal growth is promoted in specific regions of the substrate [138]. Once a film has been nucleated, the laser is turned off and the passage of further TIBA vapors over the substrate results in the formation of an Al film only in the regions which had been exposed to the laser illumination. In this way, selective area film growth of Al has been implemented using both scanning (direct writing) and projection-masked (projection lithography), laser-assisted patterning techniques [134, 139-144]. The process has been demonstrated on various substrates such as Si, SiO_2, Al_2O_3 and GaAs where a significant barrier to thermal nucleation of Al exists [140].

With a 248 nm KrF excimer laser, a substrate temperature of 250°C and TIBA pressure of approximately 100 mtorr, feature resolutions were dependent on the focusing of the UV radiation and not on gas phase diffusion lengths because the photo reactions were confined mainly to the surface adsorbate [134, 140, 141]. When 193 nm radiation was used under identical conditions, control of spatial selectivity was severely impeded indicating that substantial photo chemistry and presumably nucleation took place in the gas-phase [142, 144, 145].

The gas phase photolysis products of TIBA (and other Al CVD precursors) were sensitive to the wavelength of the radiation [146]. The metal containing decomposition products monitored in the gas phase were Al atoms and AlH [146-150]. A small but discernible increase in the yield of Al was detected at a photolysis wavelength of 193 nm over photolysis at 248 nm and may account for the loss of selectivity at the lower wavelength. In a similar study performed with trimethylaluminum (TMA), $AlCH_3$, Al and AlH were generated [151-154]. The same products were observed for the surface induced photolysis reactions on silicon and quartz [146-148]. The much higher abundance of AlH from TIBA can be from the β-hydrogen elimination. A mechanism for the surface photolysis of TIBA is similar to the one proposed for the surface pyrolysis reaction [143, 155-157].

Much of the literature on TMA [$Al(CH_3)_3$] photolysis has been reviewed [26, 28, 158]. In the far UV region (190-270 nm), TMA docomposes in the gas phase via two competing fragmentation pathways both of which involve a one-photon process for the monomer [159]. The Al containing fragments from these photo decomposition reactions are Al and $AlCH_3$ [149, 151] and the ratio of these two species is wavelength dependent [146]. Between 230-255 nm, atomic Al is produced as shown in Eq. (6) and (7) with little or no $AlCH_3$.

$$Al(CH_3)_3 + h\nu \rightarrow Al(CH_3)_2^* + CH_3 \tag{6}$$

$$Al(CH_3)_2^* \rightarrow Al + C_2H_6 \tag{7}$$

Below about 230 nm, Eq. (8) becomes increasingly important and at 190 nm the product is almost exclusively $AlCH_3$.

$$Al(CH_3)_3 + h\nu \rightarrow Al(CH_3) + CH_3 + CH_3 \tag{8}$$

It is interesting that the production of Al atoms in Eq. (7) occurs at a longer wavelength than that required to produce $AlCH_3$ due to the rapid evolution of ethane in the latter case [154].

The reaction pathway on the substrate surface [160-173] and in the gas phase [174-181] were found to be sensitive to temperature, the chemical environment, the laser power and the wavelength. For example, at low substrate temperatures CH_3 may not be readily desorbed leading to the incorporation of carbon into the film. Furthermore, rapid electronic relaxation of adsorbate molecules by the surface can make it difficult to remove carbon by a photolysis process alone [156, 182]. On the other hand, too high a substrate temperature facilitates alternative reaction pathways. These effects have resulted in Al films containing both occluded carbon and carbon directly bound to Al. The level of residual carbon is found to be sensitive to the presence of H_2 carrier which was thought to scavenge CH_3 and reactive radicals both from the gas phase and on substrate surfaces [169, 170].

Photolytically generated Al deposits can be obtained from DMAH [183-187]. Surface reactions of DMAH were induced with a deuterium lamp, an ArF laser, and an Ar ion laser. The best results were obtained with wavelengths below 200 nm on Si and

SiO_2 substrates heated above ambient temperature [186, 187]. Under these circumstances, nucleation occurred selectively on the substrate surface. For Si at temperatures of 170 and 270℃, carbon content was 2-3%. At 270℃ in the presence of irradiation from a deuterium lamp, resistivities down to 6.2 μΩ-cm were obtained. This result was compared with a resistivity of 140 μΩ-cm for a film deposited at 260℃ without irradiation. Although photolysis appeared to enhance the quality of the deposits and lower the deposition temperature, the latter value was much higher compared with the lower resistivities of other pyrolytically produced CVD films deposited in the presence of hydrogen at similar temperatures. Hydrogen may help to remove carbon from these films. The activation energy for aluminum growth on SiO_2, induced by surface photolysis and pyrolysis, was obtained and the value was found to lie in the range of 28-37 kcal/mol [188].

Photochemical CVD process has not been used widely for commercial applications because of the difficulties in depositing on large area substrates and contamination on optical windows.

CONCLUDING REMARKS

It has been shown that the chemical reaction mechanism of Al deposition is determined by the molecular structure of the precursor and the substrate surface. Also the composition and morphology of the thin film is critically dependent on the deposition mechanism. In Al CVD, rough surface morphology (sometimes 10-15% of film thickness) is observed due to the slow rate of nucleation of Al on the surface relative to the rate of Al growth. Because the growth of Al is autocatalytic, once nucleation has occurred, growth of Al takes place on the surface of the Al island more rapidly than the rate at which other islands are formed. This surface roughness can cause problems in the subsequent lithographic process.

The time to failure of the films due to rapid electromigration did not compare favorably with the corresponding values for evaporated Al-Cu alloys [39]. The electromigration resistance of CVD Al has been improved somewhat by forming Al-Si alloys. A post deposition alloying process inside a hot wall reactor has been described in which freshly deposited Al films were exposed to the vapors of SiH_4 above 250℃ in a flow of H_2 carrier gas [37]. Silane decomposed on the Al surface and was subsequently adsorbed by the film to form a solid solution up to the solubility limit at the temperature of the film. Introducing disilane (Si_2H_6) directly into the TIBA feed gas prior to its introduction into the reaction chamber eliminated the need for a post deposition stage [189-192]. The resistivity of the Al-0.4% Si films were typically 10-15% higher than for bulk Al.

The contribution of gas phase chemical reactions in Al CVD is not large but gas phase chemistry could, however, play a more significant role in the nucleation of Al films especially on insulating surfaces such as SiO_2. The observation of small numbers of Al particles in the gas phase suggests that some chemistry does occur there [193]. Gas phase particle formation is usually a serious problem in the integrated circuit processing and it should be suppressed as completely as possible. More research is needed to address this problem in Al CVD.

Topology improvement and selectivity enhancement can be achieved from the pretreatment of the substrate surface [194]. Carbon incorporation can be a problem in Al CVD and alane precursors and their synthesis has drawn much attention recently [195]. Also the use of tritertiarybutylaluminum has been reported [196]. Surface chemical reactions of precursors on various substrate materials and ensuing selectivity issues have been and will be an important research topics in Al CVD [197-200].

To develop a CVD process and equipment compatible with ULSI applications, chemistries involved in the synthesis and decomposition of precursors, chemical reaction engineering coupled with transport phenomena, materials aspect of the thin films, and electrical properties compatible with the device requirement have to be studied comprehensively.

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REFERENCES

1. Learn, A. J.: *J. Electrochem. Soc.*, **123**, 994 (1976).
2. Pramanik, D. and Saxena, A. N.: *Solid State Technol.*, **26**(1), 127 (1983).
3. Pramanik, D. and Saxena, A. N.: *Solid State Technol.*, **26**(3), 131 (1983).
4. Garosshen, T. J., Stephenson, T. A. and Slavin, T. P.: *J. Metals*, **37**(5), 55 (1985).
5. Levy, R. A. and Green, M. L.: *J. Electrochem. Soc.*, **134**, 37C (1987).
6. Pramanik, D. and Saxena, A. N.: *Solid State Technol.*, **33**(3), 73 (1990).
7. Sequeda, F. O.: *J. Metals*, **37**(5), 43 (1985).
8. Green, M. L. and Levy, R. A.: *J. Metals*, **37**(6), 63 (1985).
9. Malik, F.: *Thin Solid Films*, **206**, 70 (1991).
10. Vaidya, S. and Sinha, A. K.: *Thin Solid Films*, **75**, 253 (1981).
11. Graper, E. B.: *J. Vac. Sci. Technol.*, **8**, 333 (1971).
12. Hoffman, V.: *Solid State Technol.*, **19**(12), 57 (1976).
13. Vorous, T. V.: *Solid State Technol.*, **19**(12), 62 (1976).
14. Fuller, T. and Ghate, P. B.: *Thin Solid Films*, **64**, 25 (1979).
15. Levy, R. A., Parrillo, L. C., Lecheler, L. J. and Knoell, R. V.: *J. Electrochem. Soc.*, **132**, 159 (1985).
16. Yamada, I. and Takagi, T.: *IEEE Transactions on Electron Devices*, **34**, 1018 (1987).
17. Movchan, B. A. and Demchishin, A. V.: *Phys. Met. Metallogr.*, **28**, 83 (1969).
18. Thornton, J. A.: *J. Vac. Sci. Technol.*, **11**, 666 (1974).
19. Thornton, J. A.: *Ann. Rev. Mater. Sci.*, 7, 239 (1977).
20. Messier, R., Giri, A. P. and Roy, R. A.: *J. Vac. Sci. Technol.*, **A2**, 500 (1984).
21. Messier, R. and Yehoda, J. E.: *J. Appl. Phys.*, **58**, 3739 (1985).
22. Curran, J. E., Page, J. S. and Pick, U.: *Thin Solid Films*, **97**, 259 (1982).
23. Wan, L. J., Chen, B. Q. and Kuo, K. H.: *J. Vac. Sci. Technol.*, **A6**, 3160 (1988).
24. Raupp, G. B. and Cale, T. S.: *Chem. Mater.*, **1**, 207 (1989).
25. Cooke, M. J.: *Vacuum*, **35**, 67 (1985).
26. Herman, I. P.: *Chem. Rev.*, **89**, 1323 (1989).
27. Jensen, K. F. and Kern, W., eds.: "Thin Film Processes II", Academic Press, San Diego, p. 283 (1991).
28. Jensen, K. F. and Kern, W., eds.: "Thin Film Processes II", Academic Press, San Diego, p. 443 (1991).
29. Rhee, S. and Rhee, J.: "CVD Handbook", Bando Publishing Co. (Translated from Japanese Version into Korean), Seoul (1993).

30. Hitchman, H. and Jensen, K. F., eds.: "Chemical Vapor Deposition-Principles and Applications, Academic Press, New York (1993).
31. Jensen, K. F., Einset, E. O. and Fotiadis, D. I.: *Ann. Rev. Fluid Mech.*, **23**, 197 (1991).
32. De Croon, M. H. J. M. and Giling, L. J.: *J. Electrochem. Soc.*, **137**, 2867 (1990).
33. Moffat, H. and Jensen, K. F.: *J. Cryst. Growth*, **77**, 108 (1986).
34. Fotiadis, D. I., Kieda, S. and Jensen, K. F.: *J. Cryst. Growth*, **102**, 441 (1990).
35. Wilkinson, G., Stone, F. G. A. and Abel, E. W., eds.: "Comprehensive Organometallic Chemistry", Pergamon Press, Oxford, Vol. 1, p. 555 (1982).
36. Wiberg, E. and Amberger, E.: "Hydrides of the Elements of Main Groups I-IV", Elsevier, Amsterdam, p. 381 (1971).
37. Cooke, M. J., Heinecke, R. A., Stern, R. C. and Maes, J. W.: *Solid State Technol.*, **25**(12), 62 (1982).
38. Green, M. L., Levy, R. A., Nuzzo, R. G. and Coleman, E.: *Thin Solid Films*, **114**, 367 (1984).
39. Levy, R. A., Green, M. L. and Gallagher, P. K.: *J. Electrochem. Soc.*, **131**, 2175 (1984).
40. Powell, C. F.: "Vapor Deposition", John Wiley and Sons, New York, p. 277 (1966).
41. Kwakman, L. F. T., Sluijk, B. G., Piekaar, H. and Granneman, E. H. A.: "Tungsten and Other Refractory Metals for VLSI Applications IV", MRS, Pittsbugh, p. 315 (1989).
42. Bent, B. E., Nuzzo, R. G. and Dubois, L. H.: *J. Vac. Sci. Technol.*, **A6**, 1920 (1988).
43. Bent, B. E., Nuzzo, R. G. and Dubois, L. H.: *Mater. Res. Soc. Symp. Proc.*, **101**, 177 (1988).
44. Bent, B. E., Nuzzo, R. G. and Dubois, L. H.: *J. Amer. Chem. Soc.*, **111**, 1634 (1989).
45. Bent, B. E., Dubois, L. H. and Nuzzo, R. G.: *Mater. Res. Soc. Symp. Proc.*, **131**, 327 (1989).
46. Terao, H. and Sunakawa, H.: *J. Cryst. Growth*, **68**, 157 (1984).
47. Frese, V., Regel, G. K., Hardtddegen, H., Brauers, A., Balk, P., Hostalek, M., Lokai, M., Pohl, L., Miklis, A. and Werner, K.: *J. Elect. Mater.*, **19**, 305 (1990).
48. Bent, B. E., Nuzzo, R. G., Zegarski, B. R. and Dubois, L. H.: *J. Amer. Chem. Soc.*, **113**, 143 (1991).
49. Bent, B. E., Nuzzo, R. G., Zegarski, B. R. and Dubois, L. H.: *J. Amer. Chem. Soc.*, **113**, 1137 (1991).
50. Egger, K. W.: *J. Amer. Chem. Soc.*, **91**, 2867 (1968).
51. Egger, K. W.: *Intl. J. Chem. Kinetics*, **1**, 459 (1969).
52. Mantell, D. A.: *J. Vac. Sci. Technol.*, **A9**, 1045 (1991).
53. Mantell, D. A.: *Mater. Res. Soc. Symp. Proc.*, **131**, 357 (1989).
54. Mantell, D. A.: *J. Vac. Sci. Technol.*, **A7**, 630 (1989).
55. Higashi, G. S.: *Appl. Surf. Sci.*, **43**, 6 (1989).
56. Higashi, G. S., Raghavachari, K. and Steigerwald, M. L.: *J. Vac. Sci. Technol.*, **B8**, 103 (1990).
57. Laubengayer, A. W. and Gilliam, W. F.: *J. Amer. Chem. Soc.*, **63**, 477 (1941).
58. Coates, G. E., Green, M. L. H., Powell, P. and Wade, K.: "Principles of Organometallic Chemistry", Methuen, London, p. 36 (1971).
59. Salaneck, W. R., Bergman, R., Sundgren, J., Rockeett, A., Motooka, T. and Greene, J. E.: *Surf. Sci.*, **198**, 461 (1988).
60. Motooka, T., Rockett, A., Fons, P., Greene, J. E., Salaneck, W. R., Bergman, R. and Sundgren, J.-E.: *J. Vac. Sci. Technol.*, **A6**, 3115 (1988).
61. Motooka, T., Fons, P. and Greene, J. E.: *Mater. Res. Soc. Symp. Proc.*, **131**, 345 (1989).
62. Gow, T. R., Lin, R., Cadwell, L. A., Lee, F., Backman, A. L. and Masel, R. I.: *Chem. Mater.*, **1**, 406 (1989).
63. Biswas, D. R., Ghosh, C. and Layman, R. L.: *J. Electrochem. Soc.*, **130**, 234 (1983).
64. Squire, D. W., Dulcey, C. S. and Lin, M. C.: *J. Vac. Sci. Technol.*, **B3**, 1513 (1985).
65. Squire, D. W., Dulcey, C. S. and Lin, M. C.: *Chem. Phys. Lett.*, **116**, 525 (1985).
66. Lee, F., Gow, T. R., Lin, R., Backman, A. L., Lubben, D. and Masel, R. I.: *Mater Res. Soc. Symp. Proc.*, **131**, 339 (1989).
67. Wee, A., Murrell, A. J., French, C. L., Price, R. J., Jackman, R. B. and Foord, J. S.: *Mater. Res. Soc. Symp. Proc.*, **131**, 351 (1989).
68. Gow, T. R., Lee, F., Lin, R., Backman, A. L. and Masel, R. I.: *Vacuum*, **41**, 951 (1990).
69. Strongin, D. R. and Comita, P. B.: *Mater. Res. Soc. Symp. Proc.*, **158**, 21 (1990).
70. Strongin, D. R. and Comita, P. B.: *J. Phys. Chem.*, **95**, 1329 (1991).
71. Bartram, M. E., Michalske, T. A. and Rogers, J. W., Jr.: *J. Phys. Chem.*, **95**, 4453 (1991).
72. Zhou, Y., Henderson, M. A. and White, J. M.: *Surf. Sci.*, **221**, 160 (1989).
73. Yeddanapalli, L. M. and Schubert, C. C.: *J. Chem. Phys.*, **14**, 1 (1945).
74. Rytz-Froidevaux, Y., Salathe, R. P. and Gilgen, H. H.: *Phys. Lett.*, **84A**, 216 (1981).
75. Leys, M. R.: *Chemtronics*, **3**, 179 (1988).
76. Shanov, V., Ivanov, B. and Popov, C.: *Thin Solid Films*, **207**, 71 (1992).
77. Suzuki, N., Anayama, C., Masu, K., Tsubouchi, K. and Mikoshiba, N.: *Jpn. J. Appl. Phys.*, **25**, 1236 (1986).
78. Carlsson, J., Gorbatkin, S., Lubben, D. and Greene, J. E.: *J. Vac. Sci. Technol.*, **B9**, 2759 (1991).
79. Bhat, R., Koza, M. A., Chang, C. C. and Schwarz, S. A.: *J. Cryst. Growth*, **77**, 7 (1986).
80. Smith, W. R. and Wartik, T.: *J. Inorg. Nucl. Chem.*, **29**, 629 (1967).
81. Kobayashi, N. and Fukui, T.: *Elect. Lett.*, **20**, 887 (1984).
82. Keuch, T. F., Veuhoff, E., Kuan, T. S., Deline, V. and Potemski, R.: *J. Cryst. Growth*, **77**, 257 (1986).
83. Wartik, T. and Schlesinger, H. I.: *J. Amer. Chem. Soc.*, **75**, 835 (1953).
84. Anderson, G. A., Almenningen, A., Forgaard, F. R. and Haaland, A.: *J. Chem. Soc., Chem. Comm.*, 480 (1971).
85. Coates, G. E., Green, M. L. H. and Wade, K.: "Organometallic Compounds", Barnes and Noble, Vol. 1, p. 295 (1967).
86. Tsubouchi, K., Masu, K., Shigeeda, N., Matano, T., Hiura, Y. and Mikoshiba, N.: *Appl. Phys. Lett.*, **57**, 1221 (1990).
87. Shinzawa, T., Sugai, K., Kishida, S. and Okabayashi, H.: "Tungsten and Other Advanced Metals for VLSI/ULSI Applications", MRS, Pittsburgh, p. 377 (1990).
88. Sasaoka, C., Mori, K., Kato, Y. and Usui, A.: *Appl. Phys. Lett.*, **55**, 741 (1989).
89. Levy, R. A., Gallagher, P. K., Contolini, R. and Schrey, F.: *J. Electrochem. Soc.*, **132**, 457 (1985).
90. Ruff, J. K. and Hawthorne, M. F.: *J. Amer. Chem. Soc.*, **82**, 2141 (1960).
91. Gladfelter, W. L., Boyd, D. C. and Jensen, K. F.: *Chem. Mater.*, **1**, 339 (1989).

92. Baum, T. H., Larson, C. E. and Jackson, R. L.: *Mater. Res. Soc. Symp. Proc.*, **129**, 119 (1989).
93. Beach, D. B., Blum, S. E. and LeGoues, F. K.: *J. Vac. Sci. Technol.*, **A7**, 3117 (1989).
94. Baum, T. H., Larson, C. E. and Jackson, R. L.: *Appl. Phys. Lett.*, **55**, 1264 (1989).
95. Gross, M. E., Fleming, C. G., Cheung, K. P. and Heimbrook, L. A.: *J. Appl. Phys.*, **69**, 2589 (1991).
96. Gross, M. E., Dubois, L. H., Nuzzo, R. G. and Cheung, K. P.: *Mater. Res. Soc. Symp. Proc.*, **204**, 383 (1991).
97. Dubois, L. H., Zegarski, B. R., Gross, M. E. and Nuzzo, R. G.: *Surf. Sci.*, **244**, 89 (1991).
98. Simmonds, M. G., Gladfelter, W. L., Nagaraja, R., Szymanski, W., Ahn, K.-H. and McMurry, P. H.: *J. Vac. Sci. Technol.*, **A9**, 2782 (1991).
99. Simmonds, M. G., Phillips, E. C., Hwang, J.-W. and Gladfelter, W. L.: *Chemtronics*, **5**, 155 (1991).
100. Glass, J. A., Jr., Kher, S. and Spencer, J. T.: *Thin Solid Films*, **207**, 15 (1992).
101. Houlding, V. H. and Coons, D. E.: "Proc. 7th Annual Workshop on Tungsten and Other Advanced Metals for ULSI Applications", MRS, Pittsburgh, p. 203 (1990).
102. Gross, M. E., Cheung, K. P., Fleming, C. G., Kovalchick, J. and Heimbrook, L. A.: *J. Vac. Sci. Technol.*, **A9**, 57 (1991).
103. Hitsch, C. W. and Kniseley, R. N.: *Spectrochimi. Acta*, **19**, 1385 (1963).
104. Fraser, G. W., Greenwood, N. N. and Straughan, B. P.: *J. Chem. Soc.*, 3742 (1963).
105. Almenningen, A., Gundersen, G., Haugen, T. and Haaland, A.: *Inorg. Chem.*, 7, 1575 (1968).
106. Atwood, J. L., Bennett, F. R., Elms, F. M., Jones, C., Raston, C. L. and Robinson, K. D.: *J. Amer. Chem. Soc.*, **113**, 8183 (1991).
107. Heitsch, C. W., Nordrnan, C. E. and Prry, R. W.: *Inorg. Chem.*, **2**, 508 (1963).
108. Dubois, L. H., Zegarski, B. R., Kao, C.-T. and Nuzzo, R. G.: *Sur. Sci.*, **236**, 77 (1990).
109. Foord, J. S., Murrell, A. J., O'Hare, D., Singh, N. K., Wee, T. S. and Whitaker, T. J.: *Chemtronics*, **4**, 262 (1989).
110. Wee, A. T. S., Murrell, A. J., Singh, N. K., O'Hare, D. and Foord, J. S.: *J. Chem. Soc., Chem. Comm.*, 11 (1990).
111. Nechiporenko, G. N., Petukhova, L. B. and Rozenberg, A. S.: *Bull. Acad. Sci. USSR*, **24**, 1584 (1975).
112. Mundenar, J. M., Murphy, R., Tsuei, K. D. and Plummer, E. W.: *Chem. Phys. Lett.*, **143**, 593 (1988).
113. Paul, J.: *Phys. Rev.*, **B37**, 6164 (1988).
114. Hara, M., Domen, K., Onishi, T., Nozoye, H., Nishihara, C., Kaise, Y. and Shindo, H.: *Surf. Sci.*, **242**, 459 (1991).
115. Heitsch, C. W.: *Nature*, **195**, 995 (1962).
116. Hamilton, J. F. and Logel, P. C.: *J. Catal.*, **29**, 253 (1973).
117. Lelental, M.: *J. Electrochem. Soc.*, **120**, 1650 (1973).
118. Jarrold, M. F. and Bower, J. E.: *J. Amer. Chem. Soc.*, **110**, 70 (1988).
119. Cox, D. M., Trevor, D. J., Whetten, R. L. and Kaldor, A.: *J. Phys. Chem.*, **92**, 421 (1988).
120. Hirashita, N., Kinoshita, M., Aikawa, I. and Ajioka, T.: *Appl. Phys. Lett.*, **56**, 451 (1990).
121. Gross, M. E., Harriott, L. R. and Opila, R. L., Jr.: *J. Appl. Phys.*, **68**, 4820 (1990).
122. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T.: *Jpn. J. Appl. Phys.*, **27**, 364 (1988).
123. Kobayashi, T., Sekiguchi, A., Hosokawa, N. and Asamaki, T.: *Mater. Res. Soc. Symp. Proc.*, **131**, 363 (1989).
124. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T.: *J. Vac. Sci. Technol.*, **A8**, 2976 (1990).
125. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T.: "Tungsten and Other Advanced Metals for VLSI/ULSI Applicatons V", MRS, Pittsburgh, p. 383 (1990).
126. Kobayashi, T., Sekiguchi, A., Hosokawa, N. and Asamaki, T.: *Jpn. J. Appl. Phys.*, **27**, L1775 (1988).
127. Nishikawa, S., Tani, K. and Yamaji, T.: *J. Mater. Res.*, **7**, 345 (1992).
128. Yamada, I. and Usui, H., Tanaka, S., Dahmen, U. and Westmacott, K. H.: *J. Vac. Sci. Technol.*, **A3**, 1443 (1990).
129. Hair, M. L. and Hertl, W.: *J. Phys. Chem.*, **77**, 2070 (1973).
130. Bakardjiev, I., Majdraganova, M. and Bliznakov, G.: *J. Non-Cryst. Solids*, **20**, 349 (1976).
131. Morrow, B. A. and Hardin, A. H.: *J. Phys. Chem.*, **83**, 3135 (1979).
132. Kinney, J. B. and Staley, R. H.: *J. Phys. Chem.*, **87**, 3735 (1983).
133. Sakharovskaya, G. B., Korneev, N. N., Smirnov, N. N. and Popov, A. F.: *J. Gen. Chem. USSR*, **44**, 560 (1974).
134. Fleming, C. G., Blonder, G. E. and Higashi, G. S.: *Mater. Res. Soc. Symp. Proc.*, **101**, 183 (1988).
135. Masu, K., Tsubouchi, K., Shigeeda, N., Matano, T. and Mikoshiba, N.: *Appl. Phys. Lett.*, **56**, 1543 (1990).
136. Kato, T., Ito, T. and Maeda, M.: *J. Electrochem. Soc.*, **135**, 455 (1988).
137. Osgood, J. R. M.: *Ann. Rev. Phys. Chem.*, **34**, 77 (1983).
138. Tsao, J. Y. and Ehrlich, D. J.: *J. Cryst. Growth*, **68**, 176 (1984).
139. Tsao, J. Y. and Ehrlich, D. J.: *Appl. Phys. Lett.*, **45**, 617 (1984).
140. Higashi, G. S. and Fleming, C. G.: *Appl. Phys. Lett.*, **48**, 1051 (1986).
141. Blonder, G. E., Higashi, G. S. and Flerning, C. G.: *Appl. Phys. Lett.*, **50**, 766 (1987).
142. Higashi, G. S., Blonder, G. E., Flerning, C. G., McCrary, V. R. and Donnelly, V. M.: *J. Vac. Sci. Technol.*, **B5**, 1441 (1987).
143. Mantell, D. A.: *Appl. Phys. Lett.*, **53**, 1387 (1988).
144. Higashi, G. S.: *Chemtronics*, **4**, 123 (1989).
145. Wood, T. H., White, J. C. and Thacker, B. A.: *Appl. Phys. Lett.*, **42**, 408 (1983).
146. Zhang, Y. and Stuke, M.: *J. Cryst. Growth*, **93**, 143 (1988).
147. Zhang, Y. and Stuke, M.: *Chem. Phys. Lett.*, **149**, 310 (1988).
148. Zhang, Y. and Stuke, M.: *J. Phys. Chem.*, **93**, 4503 (1989).
149. Zhang, Y. and Stuke, M.: *Chemtronics*, **4**, 71 (1989).
150. Zhang, Y. and Stuke, M.: *Mater. Res. Soc. Symp. Proc.*, **131**, 375 (1989).
151. Zhang, Y. and Stuke, M.: *Jpn. J. Appl. Phys.*, **27**, L1349 (1988).
152. Zhang, Y. and Stuke, M.: *Chemtronics*, **3**, 230 (1988).
153. Beuerrnann, T. and Stuke, M.: *Chemtronics*, **4**, 189 (1989).
154. Beuerrnann, T. and Stuke, M.: *Chem. Phys. Lett.*, 178 (1991).
155. Mantell, D. A. and Orlowski, T. E.: *Mater. Res. Soc. Symp. Proc.*, **101**, 171 (1988).
156. Higashi, G. S.: *Appl. Surf. Sci.*, **43**, 6 (1989).
157. Higashi, G. S., Raghavachari, K. and Steigerwald, M. L.: *J. Vac. Sci. Technol.*, **B8**, 103 (1990).
158. Flicstein, J.: *Appl. Surf. Sci.*, **36**, 443 (1989).
159. Beuermann, T. and Stuke, M.: *Appl. Phys.*, **B49**, 145 (1989).
160. Ehrlich, D. J. and Osgood, J. R. M.: *Chem. Phys. Lett.*, **79**, 381 (1981).
161. Higashi, G. S., Rothberg, L. J. and Fleming, C. G.: *Chem. Phys. Lett.*, **115**, 167 (1985).

162. Higashi, G. S. and Rothberg, L. J.: *J. Vac. Sci. Technol.*, **B3**, 1460 (1985).
163. Higashi, G. S. and Rothberg, L. J.: *Appl. Phys. Lett.*, **47**, 1288 (1985).
164. Lubben, D., Motooka, T. and Greene, J. E.: *Phys. Rev.*, **B39**, 5245 (1989).
165. Lubben, D., Motooka, T., Greene, J. E., Wendelken, J. F., Sundgren, J. and Salaneck, W. R.: *Mater. Res. Soc. Symp. Proc.*, **101**, 151 (1988).
166. Motooka, T.: *Review of Laser Engineering*, **18**, 712 (1990).
167. Menon, M. and Allen, R. E.: *J. Vac. Sci. Technol.*, **B7**, 729 (1989).
168. Bouree, J. E., Flicstein, J. and Nissim, Y. I.: *Mater. Res. Soc. Symp. Proc.*, **75**, 129 (1987).
169. Bouree, J. E. and Flicstein, J.: *Mater. Res. Soc. Symp. Proc.*, **101**, 55 (1988).
170. Flicstein, J., Bouree, J. E., Bresse, J. F. and Pougnet, A. M.: *Mater. Res. Soc. Symp. Proc.*, **101**, 49 (1988).
171. Bouree, J. E., Flicstein, J., Bresse, J. F., Rommeluere, J. F. and Pougnet, A. M.: *Mater. Res. Soc. Symp. Proc.*, **129**, 251 (1989).
172. Orlowski, T. E. and Mantell, D. A.: *Mater. Res. Soc. Symp. Proc.*, **101**, 165 (1988).
173. Oprysko, M. M. and Beranek, M. W.: *J. Vac. Sci. Technol.*, **B5**, 496 (1987).
174. Solanki, R., Ritchie, W. H. and Collins, G. J.: *Appl. Phys. Lett.*, **43**, 454 (1983).
175. Motooka, T., Gorbatkin, S., Lubben, D. and Greene, J. E.: *J. Appl. Phys.*, **58**, 4397 (1985).
176. Motooka, T., gorbatkin, S., Lubben, D., Eres, D. and Greene, J. E.: *J. Vac. Sci. Technol.*, **A4**, 3146 (1986).
177. Eres, D., Motooka, T., Gorbatkin, S., Lubben, D. and Green, J. E.: *J. Vac. Sci. Technol.*, **B5**, 848 (1987).
178. Brum, J. L., Tong, P. and Koplitz, B.: *Appl. Phys. Lett.*, **56**, 695 (1990).
179. Fischer, M., Luckerath, R., Balk, P. and Richter, W.: *Chemtronics*, **3**, 156 (1988).
180. Okabe, H., Emadi-Babaki, M. K. and McCrary, V. R.: *J. Appl. Phys.*, **69**, 1730 (1991).
181. Yau, S., Saltz, D. and Nayfeh, M. H.: *Appl. Phys. Lett.*, **57**, 2913 (1990).
182. Higashi, G. S. and Steigerwald, M. L.: *Appl. Phys. Lett.*, **54**, 81 (1989).
183. Cacouris, T., Scelsi, G., Scarmozzino, R., Osgood, J. R. M. and Krchnavek, R. R.: *Mater. Res. Soc. Symp. Proc.*, **101**, 43 (1988).
184. Cacouris, T., Scelsi, G., Shaw, P., Scarmozzino, R. and Osgood, R. M.: *Appl. Phys. Lett.*, **52**, 1865 (1988).
185. Hanabusa, M., Hayakawa, K., Oikawa, A. and Maeda, K.: *Jpn. J. Appl. Phys.*, **27**, L1392 (1988).
186. Hanabusa, M., Oikawa, A. and Cai, P. Y.: *J. Appl. Phys.*, **66**, 3268 (1989).
187. Hanabusa, M. and Ikeda, M.: *Mat. Res. Soc. Symp. Proc.*, **158**, 135 (1990).
188. Scarmozzino, R., Cacouris, T. and Osgood, J. R. M.: *Mat. Res. Soc. Symp. Proc.*, **158**, 121 (1990).
189. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T.: *Jpn. J. Appl. Phys.*, **27**, 364 (1988).
190. Kobayashi, T., Sekiguchi, A., Hosokawa, N. and Asamaki, T.: *Mater. Res. Soc. Symp. Proc.*, **131**, 363 (1989).
191. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T. J.: *Vac. Sci. Technol.*, **A8**, 2976 (1990).
192. Sekiguchi, A., Kobayashi, T., Hosokawa, N. and Asamaki, T.: "Tungsten and Other Advanced Metals for VLSI/ULSI Applications V", MRS, Pittsburgh, p. 383 (1990).
193. Simmons, M. G., Gladfelter, W. L., Li, H. and McMurry, P. H.: *J. Vac. Sci. Technol.*, **A11**(6), 3026 (1993).
194. Lee, K.-I., Kim, Y.-S. and Joo, S.-K.: *J. Electrochem. Soc.*, **139**, 3578 (1992).
195. Frigo, D. M., Eijden, G. J. M., Reuvers, P. J. and Smit, C. J.: *Chem. Mater.*, **6**, 190 (1994).
196. Jones, A. C., Auld, J., Rushworth, S. A. and Critchlow, G. W.: *J. Cryst. Growth*, **135**, 285 (1994).
197. Gladfelter, W. L.: *Chem. Mater.*, **5**, 1372 (1993).
198. Simmonds, M. G., Taupin, I. and Gladfelter, W. L.: *Chem. Mater.*, **6**, 935 (1994).
199. Elms, F. M., Lamb, R. N., Pigram, P. J., Gardiner, M. G., Wood, B. J. and Raston, C. L.: *Chem. Mater.*, **6**, 1059 (1994).
200. Takeyasu, N., Kawano, Y., Kondoh, E., Katagiri, T., Yamamoto, H., Shinriki, H. and Ohta, T.: *Jpn. J. Appl. Phys.*, **33**(part 1. 1B), 424 (1994).