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The Preparation of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  Thin Films  
Using  $[\text{Al}(\text{OSiEt}_3)_3]_2$  as a Single Source Precursor

by

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## The Preparation of $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$ Thin Films Using $[\text{Al}(\text{OSiEt}_3)_3]_2$ as a Single Source Precursor

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Amorphous  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  thin films have been grown by atmospheric pressure metal-organic chemical vapor deposition using the single source precursor  $[\text{Al}(\text{OSiEt}_3)_3]_2$ . Characterization by X-ray photoelectron spectroscopy indicated that the films consisted of a mixture of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and an aluminosilicate. The relative amount of each species was dependent on the deposition temperature and the carrier gas composition. Use of  $\text{NH}_3$  as the carrier gas resulted in the increased volatility of the precursor by the *in situ* formation of the low melting Lewis acid-base adduct  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$ , however, no nitrogen incorporation was observed in these deposited films.

**Keywords:** Alumina, silica, aluminosilicate; Metal-organic chemical vapor deposition; thin film.

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## INTRODUCTION

Aluminum silicates,  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$ , are attractive candidates as corrosion and wear-resistant coatings for metals and other substrates, due to their superior properties of creep resistance, thermal expansion, and chemical stability.<sup>1</sup> Recently, it has been proposed that amorphous alumina-silica films would find application as insulators in multilevel interconnections, and as encapsulants for active devices and thin film components, because they do not suffer the temperature instability of alumina films while retaining the desirable insulating characteristics.

Thin films of aluminum silicates have been previously prepared by either sol-gel techniques<sup>2</sup> or the pyrolysis of aluminum-silicon containing polymers.<sup>3</sup> However, there remain some difficulties in obtaining homogeneous and continuous films. Metal-organic chemical vapor deposition (MOCVD) offers an attractive alternative to these methods, since contiguous, homogeneous thin films can be deposited at low temperatures with high growth rates.<sup>4</sup>

Thin films of metal oxides have previously been obtained by the pyrolytic decomposition of metal alkoxides in the vapor phase, while mixtures of two different kinds of alkoxides have been used for the formation of binary oxides.<sup>5</sup> The application of conventional MOCVD methodology for the deposition of binary oxide films suffers from stoichiometry control problems since extensive efforts must be made to control the vapor phase concentration of two precursors with often dissimilar vapor pressures. In an effort to solve this problem synthetic chemists have channelled much of their research effort in MOCVD towards the concept of developing volatile metal organic compounds, which contain all the elements required in the final deposited films. Compounds of this type have been termed single source precursors,<sup>6</sup> and have been designed, with various degrees of success, for a wide range of binary and ternary materials. The vast majority of these studies have been aimed at the preparation of electronic materials such as the III/V semiconductors where high levels of purity are of the utmost importance. By contrast, relatively little work

has been aimed at exploring the use of single source precursors for producing ceramics for structural or coating applications, where moderate levels of impurities are acceptable.<sup>7</sup> Interestingly, this latter area has quite successfully been the domain of non-volatile precursors. Given the potential of single source precursors for the preparation of ceramic films we have investigated the possibility of depositing thin amorphous films of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  from a single source precursor. A preliminary account of part of this work has been communicated.<sup>8</sup>

## EXPERIMENTAL

Thermogravimetric analyses were obtained on a Seiko 200 TG/DTA instrument using a carrier gas of ammonia, argon or oxygen. Mass spectra were obtained by using a JEOL AX-505H mass spectrometer and associated data system. An electron beam energy of 70 eV was used for EI mass spectra, with a mass resolution of 1500. Reported  $m/z$  values are for the predominant ion within the isotope pattern for each signal. IR spectra ( $4000 - 600 \text{ cm}^{-1}$ ) were recorded on a Nicolet 5ZDX-FTIR spectrometer as Nujol mulls on KBr plates.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AM-500 spectrometer, and chemical shifts are reported relative to  $\text{SiMe}_4$  in  $\text{CDCl}_3$ .  $^{17}\text{O}$ ,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker WM-300 spectrometer and chemical shifts are reported versus  $\text{H}_2\text{O}$ ,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{SiMe}_4(\text{CDCl}_3)$  respectively. XPS were collected on a Surface Science Instruments Spectrometer (Model SSX-100) with a monochromatized  $\text{Al-K}\alpha$  source. The spectra were acquired with a 100 eV pass energy and a  $1000 \mu\text{m}$  spot size. Radiation damage was insignificant over the acquisition times used. All samples were sputtered with 3 keV Argon ions prior to data collection to remove adventitious carbon. Since the films were insulating, they became electrostatically charged due to the non compensation of emitted photo- and secondary-electrons. Artifacts of charging include peak shift and peak broadening. Thus, extensive charge referencing was required. All spectra were charge referenced independently to graphitic carbon ( $\text{C}_{1s} = 284.8 \pm 0.1 \text{ eV}$ ), and gold

( $Au_{4f} = 84.0 \pm 0.1$  eV). TEM was performed on a Philips EM420 analytical electron microscope operating at 120 kV. SEM studies were performed on a JEOL JSM-35 scanning microscope. AES was carried out on a Perkin-Elmer SAM-660.

Unless otherwise stated all manipulations were carried out under a nitrogen atmosphere. Solvents were dried over sodium under nitrogen, and degassed prior to use.  $Et_3SiOH$  (Huls),  $AlMe_3$  (2M solution in hexane, Aldrich) and  $NH_3$  (Matheson) were commercial samples, and were used without further purification.

### Synthesis of $[Al(OSiEt_3)_3]_2$

Trimethylaluminum (54.3 mL, 109 mmol, in a 2M hexane solution) was transferred *via* cannula into 80 mL of  $Et_2O$ , then cooled to  $-15^\circ C$ . An  $Et_2O$  (80 mL) solution of triethylsilanol (43.16 g, 327 mmol) was then slowly added to the  $AlMe_3$  solution. The methane gas produced by the reaction was vented through a bubbler to avoid an increase in pressure. Once gas evolution had ceased, the reaction was stirred overnight. Removal of the solvents in *vacuo* provided 39.45 g (94 mmol, 86.2%) of a white, waxy solid. The product is hygroscopic and should be stored under argon. Mass spectrum:  $m/z$  (EI) 840 ( $2M^+$ ), 811 ( $2M^+ - Et$ ). IR ( $cm^{-1}$ ): 1592 (w), 1414 (m), 1260 (w), 1239 (s), 1065 (vs), 1017 (s), 973 (m), 808 (vs), 782 (w), 737 (vs), 689 (vw), 670 (w), 638 (s), 585 (m), 551 (m), 500 (w). NMR ( $\delta$ ,  $C_6D_6$ ):  $^1H$  1.14 [6H, t,  $J(H-H) = 8.0$  Hz,  $CH_2CH_3$  terminal], 1.04 [3H, t,  $J(H-H) = 7.6$  Hz,  $CH_2CH_3$  bridging], 0.92 [2H, q,  $J(H-H) = 7.6$  Hz  $CH_2$  bridging], 0.76 [4H, q,  $J(H-H) = 8.0$  Hz,  $CH_2$  terminal];  $^{13}C$  7.81 [s, with  $^{29}Si$  satellites  $J(Si-C) = 59.2$  Hz,  $CH_2$  terminal], 7.79 ( $CH_3$ , terminal), 7.11 ( $CH_3$  bridging), 6.83 [s, with  $^{29}Si$  satellites  $J(Si-C) = 58.7$  Hz,  $CH_2$  bridging].  $^{17}O$  30.3 (bridging), 15.8 (terminal).  $^{27}Al$  57.1 ( $w^{1/2} = 4400$  Hz).  $^{29}Si$  25.5 (bridging), 5.6 (terminal).

### Synthesis of $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$

Solid  $[\text{Al}(\text{OSiEt}_3)_3]_2$  (2.00 g, 2.38 mmol) was exposed to a static  $\text{NH}_3$  atmosphere (760 mmHg) for 30 min. The solid rapidly softened and liquified. Removal of the ammonia under vacuum gave a low melting solid: yield 1.72 g (3.95 mmol, 83 %). Mass spectrum:  $m/z$  (CI,  $\text{NH}_3$ ) 437 ( $\text{M}^+$ ). IR ( $\text{cm}^{-1}$ ): 3641 (m), 3367 (w), 3127 (s), 2909 (s), 1614 (m), 1593 (m), 1459 (m), 1417 (m), 1382 (w), 1311 (m), 1234 (m), 1016 (vs), 805 (m), 720 (vs), 636 (m), 551 (m). NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ):  $^1\text{H}$  1.14 [27H, t,  $J(\text{H-H}) = 7.9$  Hz,  $\text{CH}_2\text{CH}_3$ ], 0.68 [18H, q,  $J(\text{H-H}) = 7.9$  Hz,  $\text{CH}_2$ ], 1.24 (3H, s,  $\text{NH}_3$ );  $^{13}\text{C}$ , 8.37 ( $\text{CH}_2$  and  $\text{CH}_2\text{CH}_3$ );  $^{17}\text{O}$ , 16.1;  $^{27}\text{Al}$  58.1 ( $w^{1/2} = 2400$  Hz);  $^{29}\text{Si}$  2.93.

### Chemical Vapor Deposition Studies

Depositions were carried out in an atmospheric pressure laminar-flow hot wall glass reactor, shown as a schematic in Figure 1. Ultra pure helium was passed through a Nanochem gas purifier (Model L-50t) prior to entry into the chamber (Figure 1, H). Oxygen and ammonia were used as supplied.

Prior to deposition experiments, the chamber was disconnected from the apparatus and cleaned thoroughly with dilute HF to remove any residue from previous runs. It was then dried with compressed air. The CVD system (Figure 1), loaded with substrates, was purged for at least 2 hours prior to deposition during which time the nickel hot plate (D) was brought to the deposition temperature (420, 470 or 550°C). Outflow from the reaction chamber exited via a latex prophylactic sheath (Trojan<sup>®</sup>) to an oil bubbler, which prevented back flow of air into the reaction chamber.

Once the chamber was brought to the desired temperature for deposition, approximately 500 mg of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  was added through the top of the chamber (G) to the area over the second hot plate (F). The chamber was closed with a septum over the inlet G and the hot plate F was set at a temperature of 220-250°C. After each deposition the films were allowed to cool in the reactor under a flow of the carrier gas.

Deposition was carried out on p-type (100) oriented silicon wafers, graphitic carbon, KBr wafers, niobium and aluminum metal, all of which were cleaned with  $\text{CH}_2\text{Cl}_2$  prior to use. Flow rates, carrier gas compositions and deposition temperatures are given in the text and Table 1.

## RESULTS AND DISCUSSION

### *Precursors: design and synthesis*

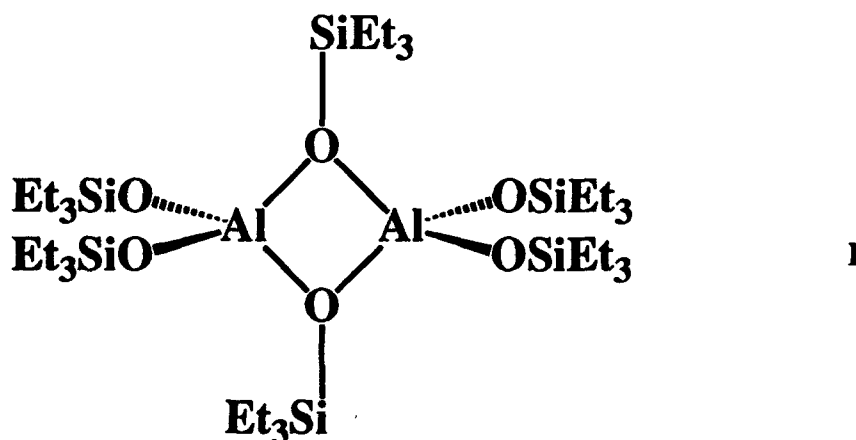
The following properties are among those that must be considered when selecting suitable candidates for a MOCVD precursor: <sup>9</sup>(a) The precursor should be either a liquid, or a solid with sufficient vapor pressure and rate of mass transport at the desired temperature; (b) the precursor should be chemically and thermally stable at its evaporation temperature, even after prolonged heating, and (c) the precursor should be relatively easy to synthesize, ensuring sufficient availability for testing and fabrication. It is also important that the synthesis of the compound be reproducible. Previous work on single source precursors<sup>10</sup> has employed the mono-siloxide complex  $\text{Al}(\text{O}^i\text{Pr})_2(\text{OSiMe}_3)$ , which does indeed meet the above requirements. It was found that except for deposition at very high temperatures ( $>900^\circ\text{C}$ ) the deposited films from the above precursor were aluminum rich ( $1.3 < \text{Al}:\text{Si} < 2.1$ ), and thus showed thermal instability of the insulating qualities caused by crystallization in the films. Thus, if a single source precursor is to be used for the deposition of silicon rich films then a greater number of preformed Al-O-Si bonds are presumably required. It is with this goal that we have investigated the use of the *tris*-siloxo aluminum complex,  $[\text{Al}(\text{OSiEt}_3)_3]_2$ .

The synthesis of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  is readily accomplished in high yield by the reaction of trimethylaluminum with  $\text{Et}_3\text{SiOH}$  in  $\text{Et}_2\text{O}$  at  $-15^\circ\text{C}$  (Eq. 1).





As is common for siloxide and alkoxide complexes of aluminum,<sup>11</sup>  $[\text{Al}(\text{OSiEt}_3)_3]_2$  exists as a dimer, **I**, both in solution and the gas phase, as determined by osmometry and mass spectroscopy (see Experimental) respectively.<sup>8</sup>



The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$  and  $^{29}\text{Si}$  NMR spectra of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  (see Experimental) are consistent with the presence of both bridging and terminal siloxy groups, in a ratio of 1:2. The unequivocal assignment of the terminal siloxy resonances was made by comparison with the respective spectra for  $\text{Al}(\text{OSiEt}_3)_3$  (L) (L=Lewis base) in which only terminal siloxy groups are present.<sup>12</sup> The  $^{27}\text{Al}$  spectra of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  is consistent with four-coordinate aluminum centers.<sup>13</sup>

$[\text{Al}(\text{OSiEt}_3)_3]_2$  is moderately air stable, but is susceptible to hydrolysis over several hours. It sublimes readily ( $220^\circ\text{C}$ , 760 mmHg) without significant decomposition (see Figure 2).

Although other *tris*-siloxide compounds were prepared, including the dimeric  $[\text{Al}(\text{OSiMe}_2^t\text{Bu})_3]_2$  and the monomeric  $\text{Al}(\text{OSiPh}_3)_3(\text{THF})$ ,<sup>14</sup> no significant volatility was observed for either. However, it should be noted that the solid state pyrolysis of both the above compounds does lead to the formation of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$ .<sup>15</sup>

### *Deposition Studies.*

Thin film growth was carried out primarily on p-type (100) oriented silicon substrates, in a resistively heated horizontal laminar flow glass MOCVD system operated at atmospheric pressure (see Experimental and Table I). In our initial studies <sup>8</sup> oxygen was used as the carrier gas to ensure complete oxidation of the deposited film. However, over the film growth time (*ca* 60 min), and at its sublimation temperature, 220-250°C, slow decomposition of the precursor,  $[\text{Al}(\text{OSiEt}_3)_3]_2$ , was observed. In order to circumvent this problem ultra-pure helium was chosen as the carrier gas. While this arrests the premature decomposition of the precursor, the deposited films were found to contain significant carbon impurities (see below). We therefore carried out a series of deposition studies at 420, 470 and 550°C with carrier gas composition of 100, 70, 30 and 0% oxygen by volume. The balance of the carrier gas mixture was ultra pure helium. From these studies, the effects of carrier gas composition on the composition of the film could be determined.

All the deposited films adhere well to the silicon substrate (Scotch tape test), and are smooth and featureless when examined by scanning electron microscopy (SEM). X-ray diffraction studies indicate that the deposited films are essentially amorphous, and no crystallinity was observed upon annealing at 800 °C for several hours. The films' resistivity at 100 V was essentially independent of carrier gas, and was in all cases larger than  $10^{12} \Omega \text{cm}$ .

The elemental composition of the films, determined by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), was found to be dependent on both temperature and the oxygen content of the carrier gas. Variation within a film or between repetitive runs was approximately  $\pm 10\%$ . Figure 3 shows the Al:Si ratio as a function of carrier gas composition for deposition at (a) 420 (b) 470 and (c) 550°C. The elemental composition of the films deposited under pure oxygen carrier gas is essentially independent of temperature, i.e. the Al:Si ratio decreases from 1.01 at 420°C to 0.80 at 550°C. This decrease in the Al:Si ratio with increasing temperature becomes more distinct

with decreasing oxygen content of the carrier gas, until at 0% O<sub>2</sub> the Al:Si ratio varies between 2.02 at 420°C and 0.66 at 550°C, a range of 300% from the smallest to the largest Al:Si ratio. This temperature and oxygen dependent variation in the film composition would suggest that two competing precursor decomposition pathways are present. The first, under 0% O<sub>2</sub> (100% He) is similar to that observed for the decomposition of Al(O<sup>i</sup>Pr)<sub>2</sub>(OSiMe<sub>3</sub>) under N<sub>2</sub>, and would imply that the film composition is determined by the temperature dependent tendencies of the Al-O-Si bonds to cleave; higher temperatures result in a greater proportion of the Al-O-Si bonds being cleaved, and consequently a lower Al:Si ratio. The second pathway must involve the temperature independent oxidative decomposition of the precursor. Further studies are in progress to elucidate the intimate details of the decomposition processes, however, we note that the Al:Si ratio is unfortunately not directly controlled by the number of siloxy ligands per aluminum in the precursor.

AES sputter depth profiles indicate a uniform composition throughout each film. However, films deposited on silicon do show segregation of silicon to the surface upon annealing at 900°C.

The surface of all the films contained significant adventitious carbon contamination (XPS), which in the case of those films deposited under 100% O<sub>2</sub> is readily removed by ion-beam sputtering (Ar<sup>+</sup>, 3keV, 1 min). The bulk films show negligible carbon content by AES (Figure 4) and XPS, while transmission infrared spectra confirm the absence of hydrocarbon impurities. In contrast to the films deposited under 100% O<sub>2</sub> carrier gas, those grown using 70, 30 and 0% oxygen (balance helium) all contain carbon impurities throughout the film, as determined by AES and XPS. The carbon content increases with decreasing oxygen content in the carrier gas, suggesting that the carbon is due to unoxidized ligand residues (see below).

Nakaido and Toyoshima have previously observed<sup>10</sup> that films grown from the single source precursor Al(O<sup>i</sup>Pr)<sub>2</sub>(OSiMe<sub>3</sub>) crystallize to triclinic kyanite, Al<sub>2</sub>SiO<sub>5</sub>, whereas those grown from a vapor phase mixture of Al(O<sup>i</sup>Pr)<sub>3</sub> and Si(OEt)<sub>4</sub> remained

amorphous even after annealing. This predisposition to crystallization in the films formed from a single source precursor is undoubtedly due to the retention of a significant number of Al-O-Si units from the precursor molecule in the deposited film. Thus the films may be thought of as containing an aluminosilicate, in addition to alumina and silica. In order to probe this possibility, and to chemically characterize the nature of the carbon residue, we have determined the high resolution XPS scans for the Al 2p, Si 2p and O 1s regions of the deposited films.

The high resolution XPS scan of the Al 2p region for all of the films shows a single asymmetric peak, a representative example of which is shown in Figure 5. The peaks for all the films may be curve fitted to consist of two peaks, which by comparison with literature values<sup>16</sup> and standard samples are attributed to  $\text{Al}_2\text{O}_3$  ( $74.3 \pm 0.1$  eV) and an aluminosilicate ( $75.7 \pm 0.2$  eV). The relative quantity of each species is dependent on both the deposition temperature, and the oxygen content of the carrier gas. Thus, the aluminosilicate content of the films is increased with higher deposition temperatures and also higher percentages of oxygen in the carrier gas mixture.

The high resolution XPS signal for the Si 2p region of the films deposited under 100% oxygen can also be line-fitted to two species (see Figure 6a),  $\text{SiO}_2$  ( $103.3 \pm 0.1$  eV) and an aluminosilicate ( $102.2 \pm 0.2$  eV). As with the Al 2p region the relative percentage of these species is found to be strongly dependent on the deposition temperature. Increased deposition temperatures results in higher aluminosilicate content relative to  $\text{SiO}_2$ . Figure 7 shows the temperature dependence of the film composition, as determined from XPS, of the films deposited under 100%  $\text{O}_2$ . Post deposition annealing of the films ( $650^\circ\text{C}$ ,  $10^{-5}$  mmHg) also results in an increase in the amount of aluminosilicate, relative to both  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . The high resolution Si 2p XP spectral component for the films deposited under either pure helium or He/ $\text{O}_2$  mixtures are consistent with the presence of a third species (Figure 6b) at low binding energy ( $101.0 \pm 0.2$  eV). Since this component increases in relative intensity (e.g. see Figure 8) with decreasing carrier gas oxygen content, we assign

it to the organic silicon residue from the precursor. Interestingly, the peak shift for this organic material is identical to that observed for the Si 2p XP spectra of siloxy-substituted alumoxanes,  $[\text{Al}(\text{O})(\text{OH})_x(\text{OSiEt}_3)_{1-x}]_n$ .<sup>12</sup>

The organic content of the film is readily eliminated by annealing the films at 800°C in air for 2h. Figure 6c shows the high resolution Si 2p XP spectral component for the films deposited under He at 550°C (Figure 6b), and then subsequently annealed in air at 800°C. It is clear that the organic silicon content is reduced while the relative amount of aluminosilicate increases. This increase in the Al-O-Si units is in agreement with our proposal that the organic residue within the films is due to unoxidized Al-O-SiEt<sub>x</sub> groups.

TEM studies on freshly deposited films also present evidence for the presence and distribution of the residual organics identified above. Electron beam interactions of a focused probe with the material resulted in the "balling-up" and subsequent elimination of the heated section of the film. Electron micrographs of this film obtained under conditions of low beam current (Figure 9a) are found to exhibit a fine structure consisting of amorphous particles of ca. 75 Å. This structure largely disappears after either room temperature aging (3 months) or oxidation, as displayed by Figure 9b; the final amorphous film being stable under similar condition of electron analysis. The TEM analysis thus suggests that the as-deposited films exist as amorphous particles of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  surrounded by an organic ligand residue. Furthermore, some form of film consolidation by oxidation and/or hydrolysis of this organic residue occurs at room temperature.

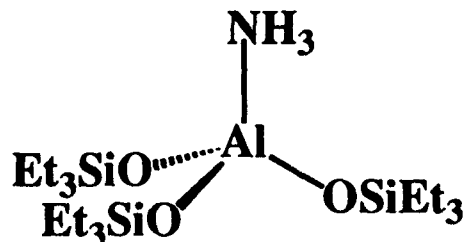
Although the majority of the deposition studies have been performed on Si substrates we have successfully grown  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  thin films on metal surfaces, as well as on graphitic carbon. It should be noted however, that no deposition is observed on either borosilicate glass or single crystal quartz substrates. At present we do not understand this anomaly, but it is under further investigation.

*Increased volatility of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  by the use of ammonia as the carrier gas.*

Despite the suitability of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  as a single source precursor for the growth of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  thin films, there remain two inherent problems. First, although  $[\text{Al}(\text{OSiEt}_3)_3]_2$  sublimates at temperatures as low as  $220^\circ\text{C}$ , higher temperatures are required to obtain reasonable mass transport rates. Second,  $[\text{Al}(\text{OSiEt}_3)_3]_2$  is a solid and does not melt before sublimation. Thus, its vapor pressure is variable depending on surface area and particle size.

There are two possible solutions to these problems. First, an alternative liquid or low-melting solid precursor could be developed. Second, a method for increasing the volatility of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  could be developed. In line with the latter option we have previously reported that the limited volatility of substituted  $\beta$ -diketonate complexes of barium, e.g.  $[\text{Ba}(\text{tmhd})_2]_\infty$  (tmhd = 2,2,6,6-tetramethylheptane -3,5-dionate), can be increased by the addition of nitrogen Lewis bases to the CVD carrier gas.<sup>17</sup> Since it has recently been determined by Rees and co-workers<sup>18</sup> that this is due to the cleavage of the oligomeric structure and the formation of a novel low molecularity complex  $[\text{Ba}(\text{tmhd})_2 \cdot 2\text{NH}_3]_2$ , we have investigated the effect of ammonia carrier gas on the volatility of  $[\text{Al}(\text{OSiEt}_3)_3]_2$ .

The addition of excess  $\text{NH}_3$  to  $[\text{Al}(\text{OSiEt}_3)_3]_2$  results in the quantitative formation of the Lewis acid-base complex  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$  (**II**), as determined from NMR and mass spectroscopy.



Heating  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$  under an inert atmosphere results in the slow loss of the coordinated  $\text{NH}_3$  and the reformation of solid  $[\text{Al}(\text{OSiEt}_3)_3]_2$ . Thus, despite its low melting point  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$  cannot itself readily be used as a volatile precursor. If, however,  $\text{NH}_3$  is used as the carrier gas  $[\text{Al}(\text{OSiEt}_3)_3]_2$  rapidly melts, forming  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$ , and enhanced mass transport is observed (Figure 1c). Since ammonia has previously been employed as a reactive source of nitrogen in the growth of nitride films,<sup>19</sup> it is conceivable that the use of  $\text{NH}_3$  as a carrier gas would result in nitrogen incorporation into the films, and the possible formation of  $\text{AlN}$ ,  $\text{Si}_3\text{N}_4$  or  $\text{SiAlON}$ . However, while XPS measurements on thin films of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  grown under  $\text{NH}_3$  indicate the total absence of nitrogen, the Al:Si ratio in films grown at  $550^\circ\text{C}$  under  $\text{NH}_3$  is significantly higher (3.0) than that observed for films grown under oxygen (0.58) or He (0.66). The low silicon content would suggest that  $\text{NH}_3$  reacts with the precursor to cleave the Al-O-Si unit, since no nitrogen is incorporated into the film. This may result in the the formation of a volatile silylamide such as  $\text{H}_2\text{NSiEt}_3$ .

## CONCLUSION

In summary, thin films of  $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y$  have been successfully prepared on silicon substrates by MOCVD at atmospheric pressure using  $[\text{Al}(\text{OSiEt}_3)_3]_2$  as a single source precursor. The chemical composition of the films is strongly dependent on the growth temperature and the choice of carrier gas, but not on the number of siloxide ligands in the precursor. The volatility of  $[\text{Al}(\text{OSiEt}_3)_3]_2$  is dramatically increased by the use of  $\text{NH}_3$  as the carrier gas, *via* the *in situ* formation of the monomeric Lewis acid-base adduct  $\text{Al}(\text{OSiEt}_3)_3(\text{NH}_3)$ .

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## Legends for Figures

**Figure 1.** CVD system using a rectangular glass tube for the reaction: A, substrate; B, glass tube; C, precursor holder; D, nickel hot plate  $T_{\max} = 800^{\circ}\text{C}$ ; E, insulation; F, second hot plate to volatilize precursor; G, inlet for precursor; H, carrier gas inlet; I, gas outlet.

**Figure 2.** Thermogravimetric analysis of  $[\text{Al}(\text{OSiEt}_3)_2]_2$  under (a) argon, (b) oxygen and (c) ammonia carrier gas.

**Figure 3.** A plot of the dependence of the Al:Si ratio within aluminum-silicate films as a function of oxygen/helium carrier gas composition ( $\%\text{O}_2$ ), deposited at (a) 420, (b) 470 and (c) 550°C.

**Figure 4.** AES spectra of the aluminum-silicate films deposited at 420°C under oxygen.

**Figure 5.** The Al 2p curve fitted XP spectra component for the alumina-silica film deposited at 420 °C under 100% He. Peak positions (eV) and assignments are included.

**Figure 6.** The Si 2p curve fitted XP spectra components for the aluminum silicate films deposited at 550°C, 100%  $\text{O}_2$  (a); 550°C, 100% He (b) and 550°C, 100% He after annealing in air at 800 °C for 2 h, (c).

**Figure 7.** Film composition from high-resolution XP spectra, of aluminum silicate thin films deposited under 100%  $\text{O}_2$  carrier gas, as a function of deposition temperature; (a) alumina, (b) silica, and (c) aluminosilicate.

**Figure 8.** Film composition from the high-resolution Si 2p curve fitted XP spectral component for the aluminum silicate film, deposited at 420°C, as a function of the carrier gas composition (% O<sub>2</sub>); (a) aluminosilicate, (b) organic silicon, and (c) silica.

**Figure 9.** Bright-field electron micrographs showing; (a) as deposited film, and (b) the same film after aging.

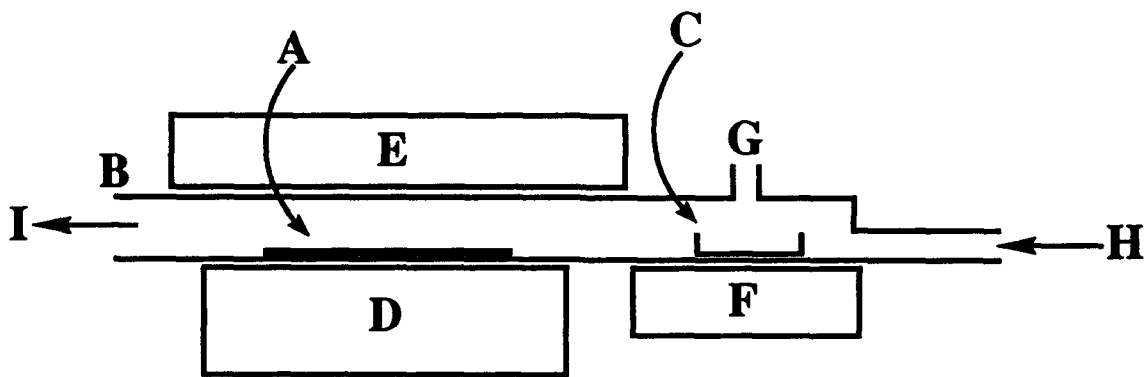


Fig 2

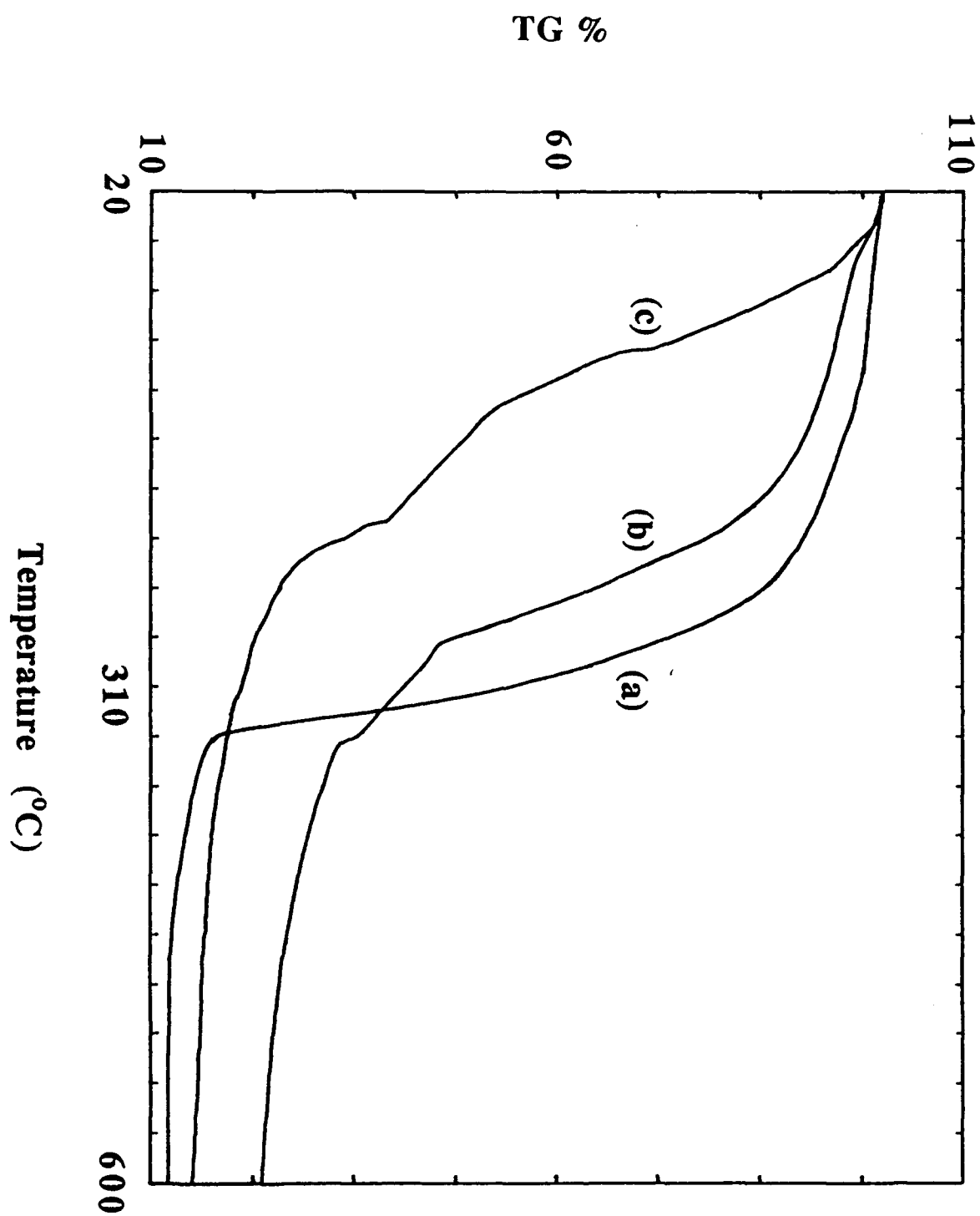


Fig 3

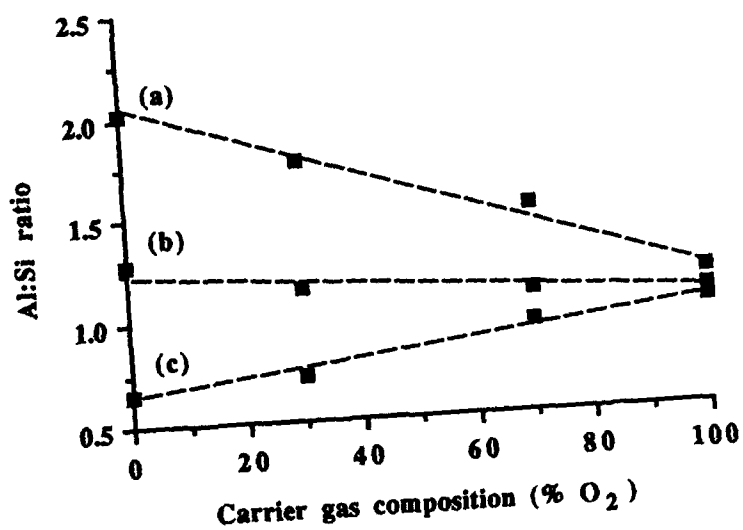
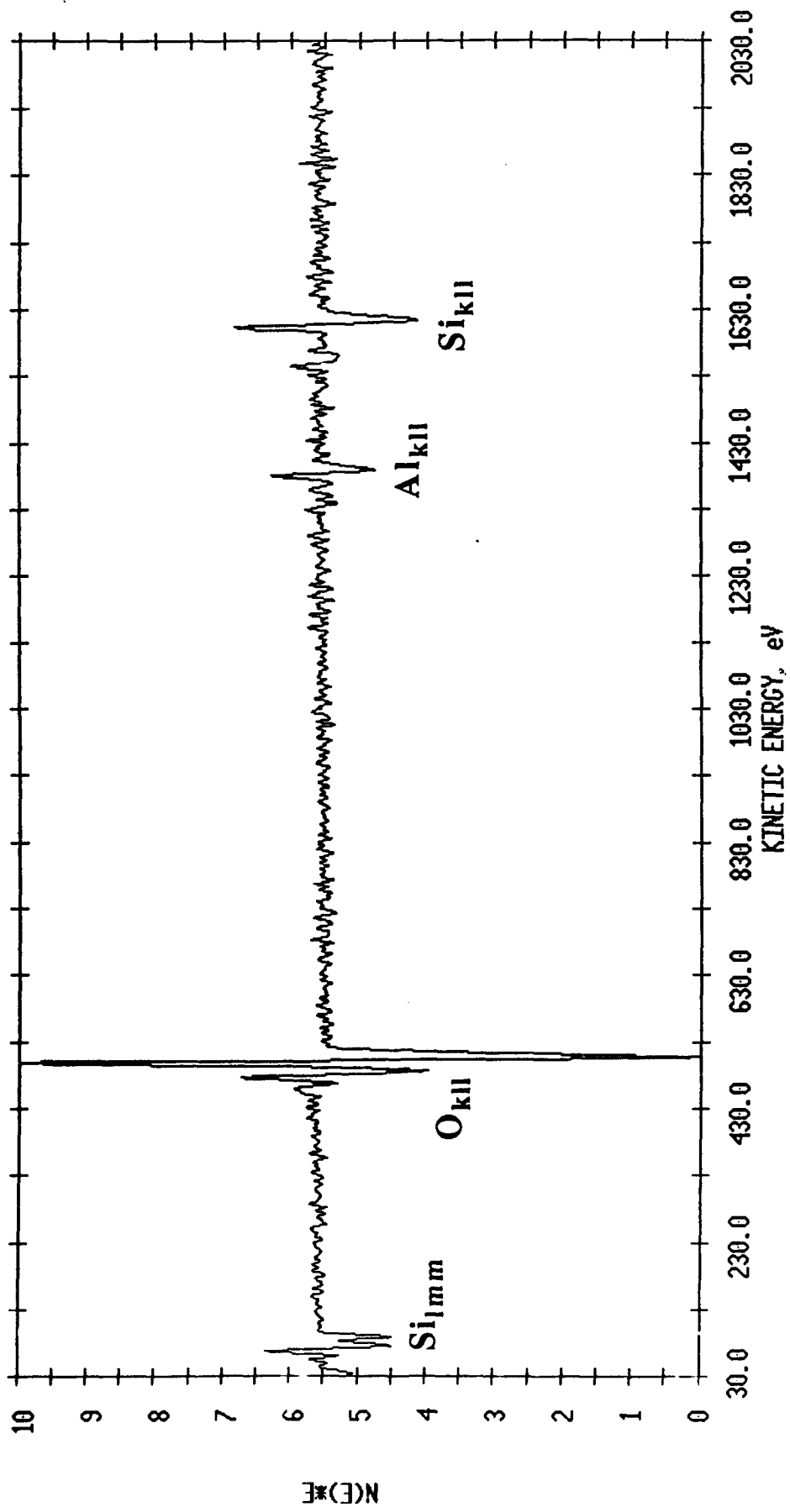




Fig 4



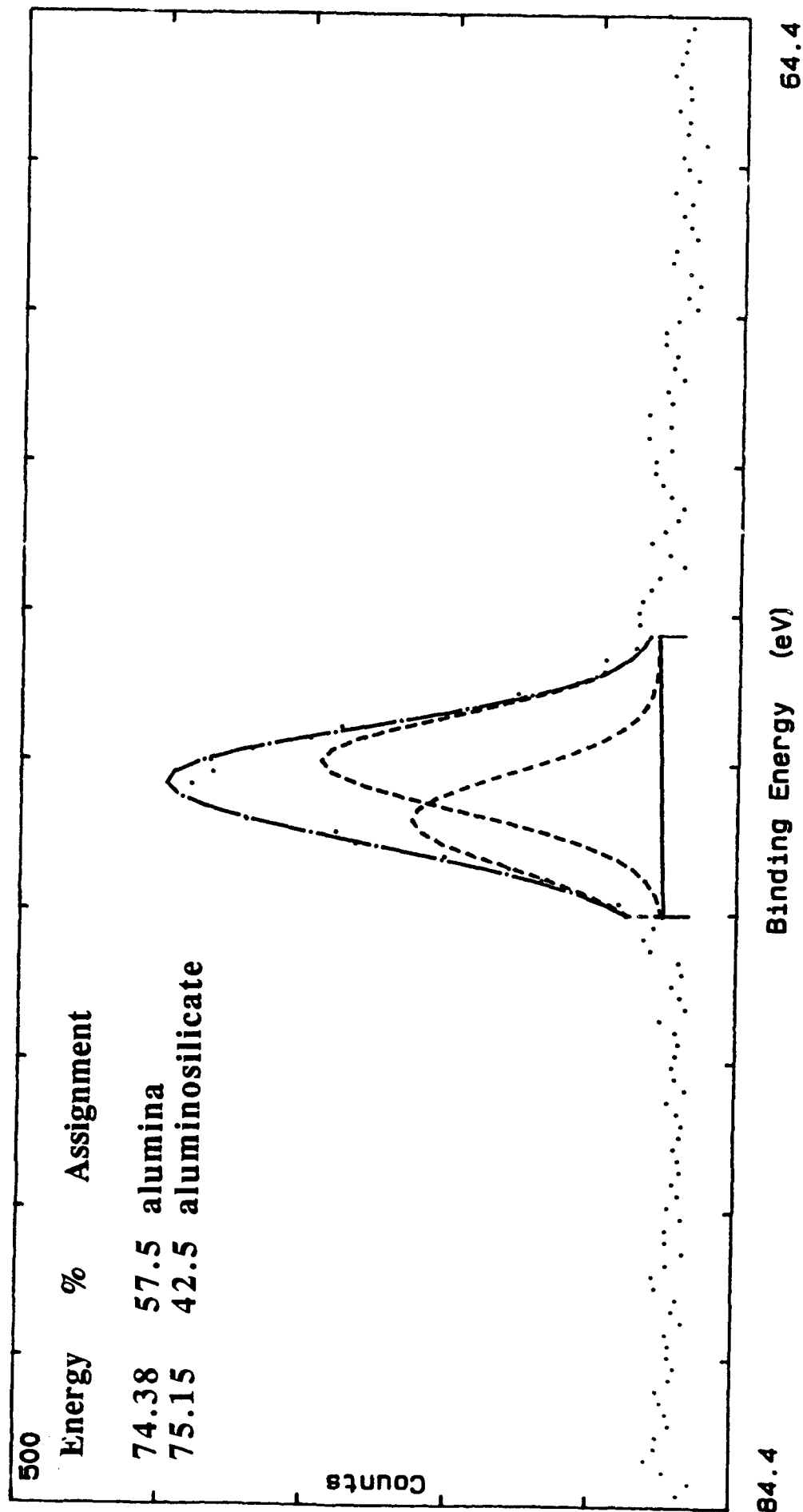


Fig 6a

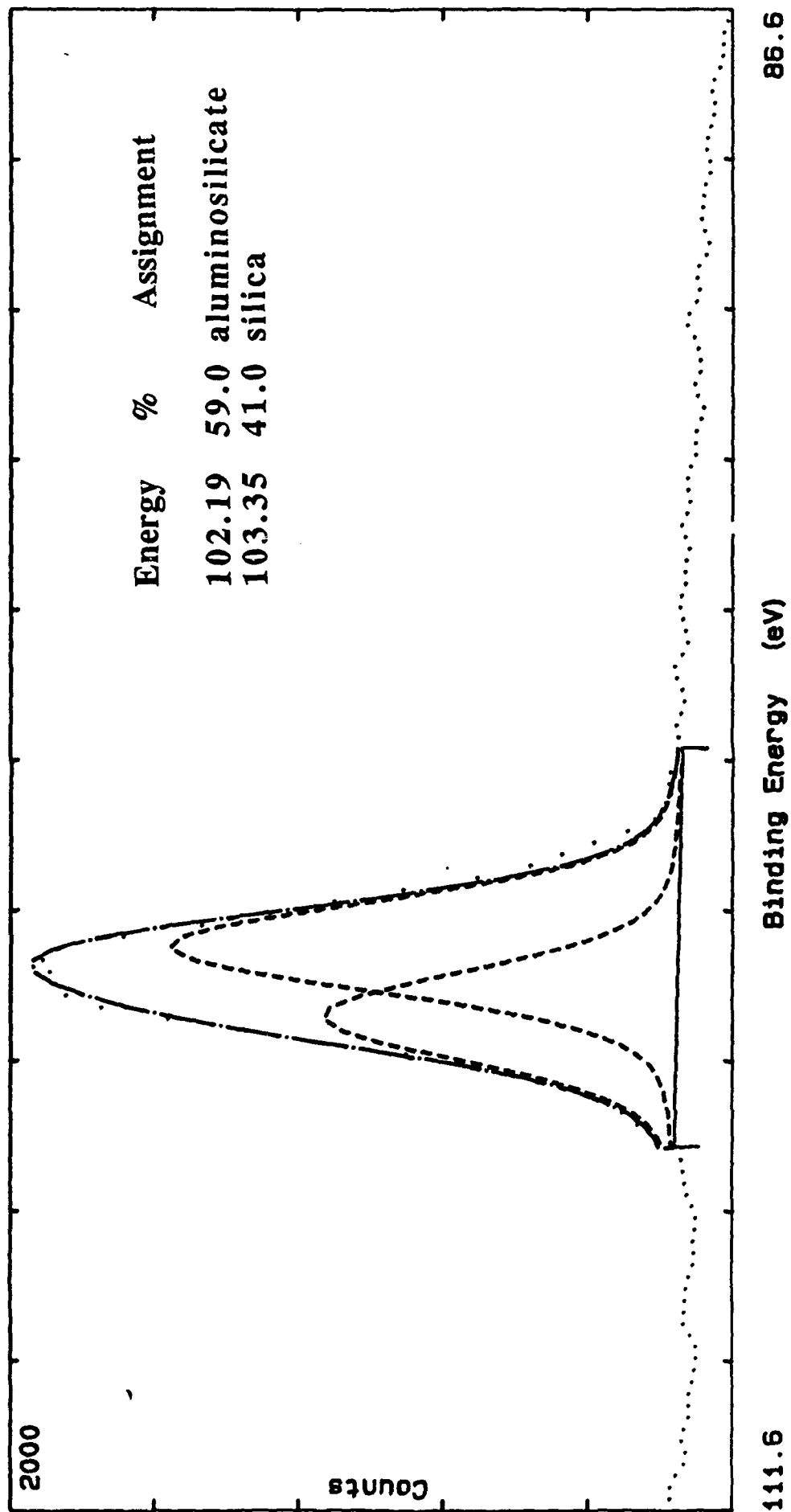


Fig 66

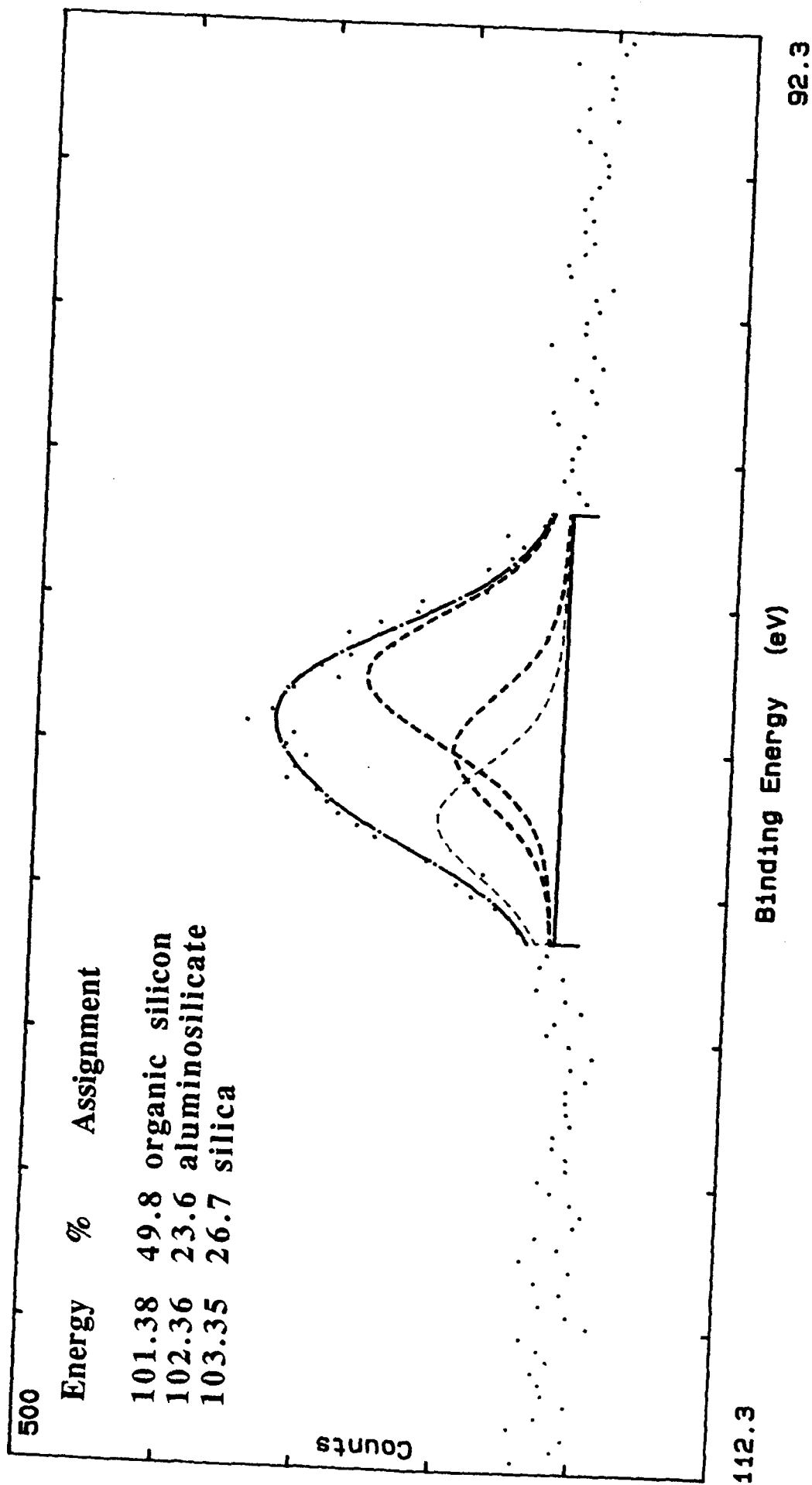


Fig 6c

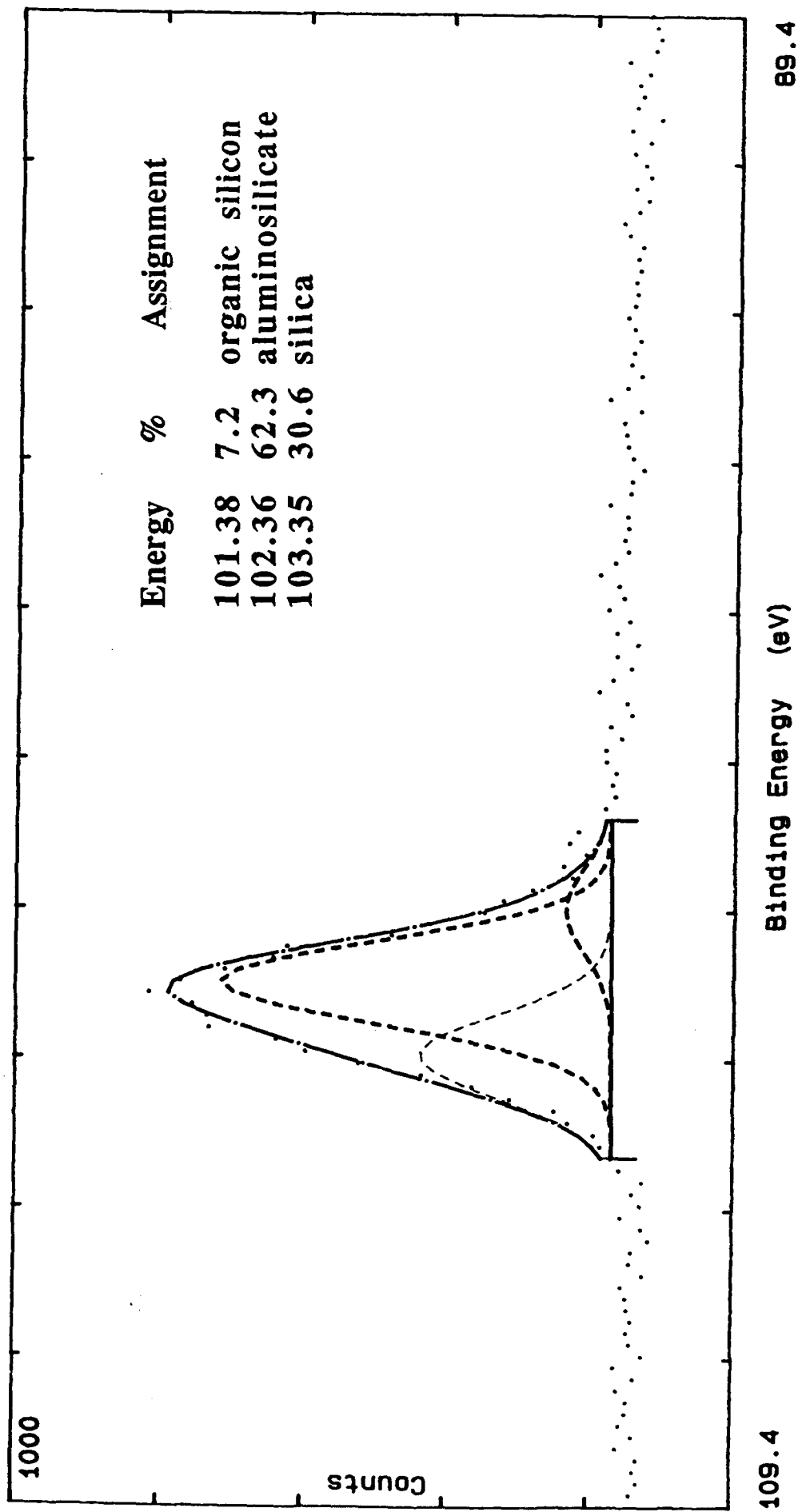


Fig 7

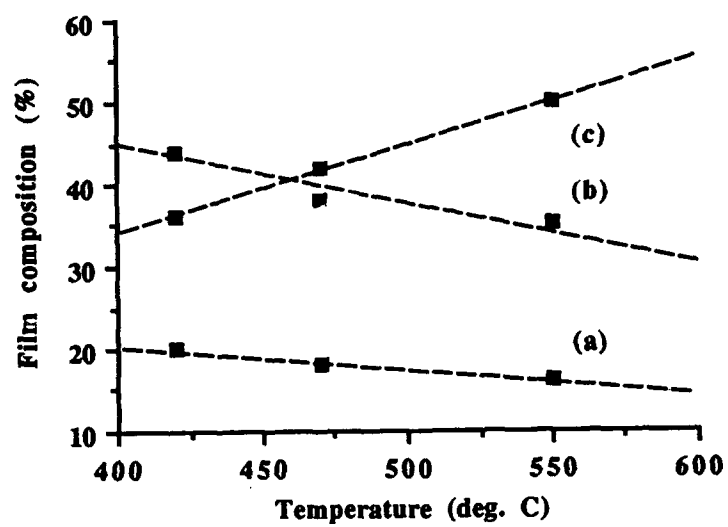


Fig 8

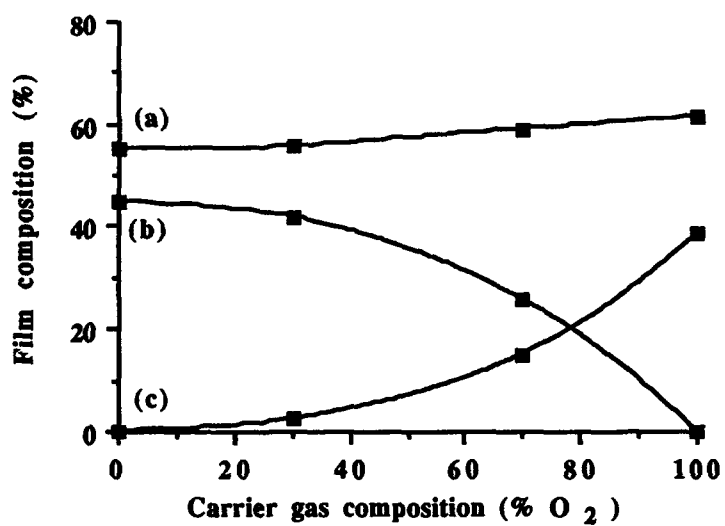


Fig 9a

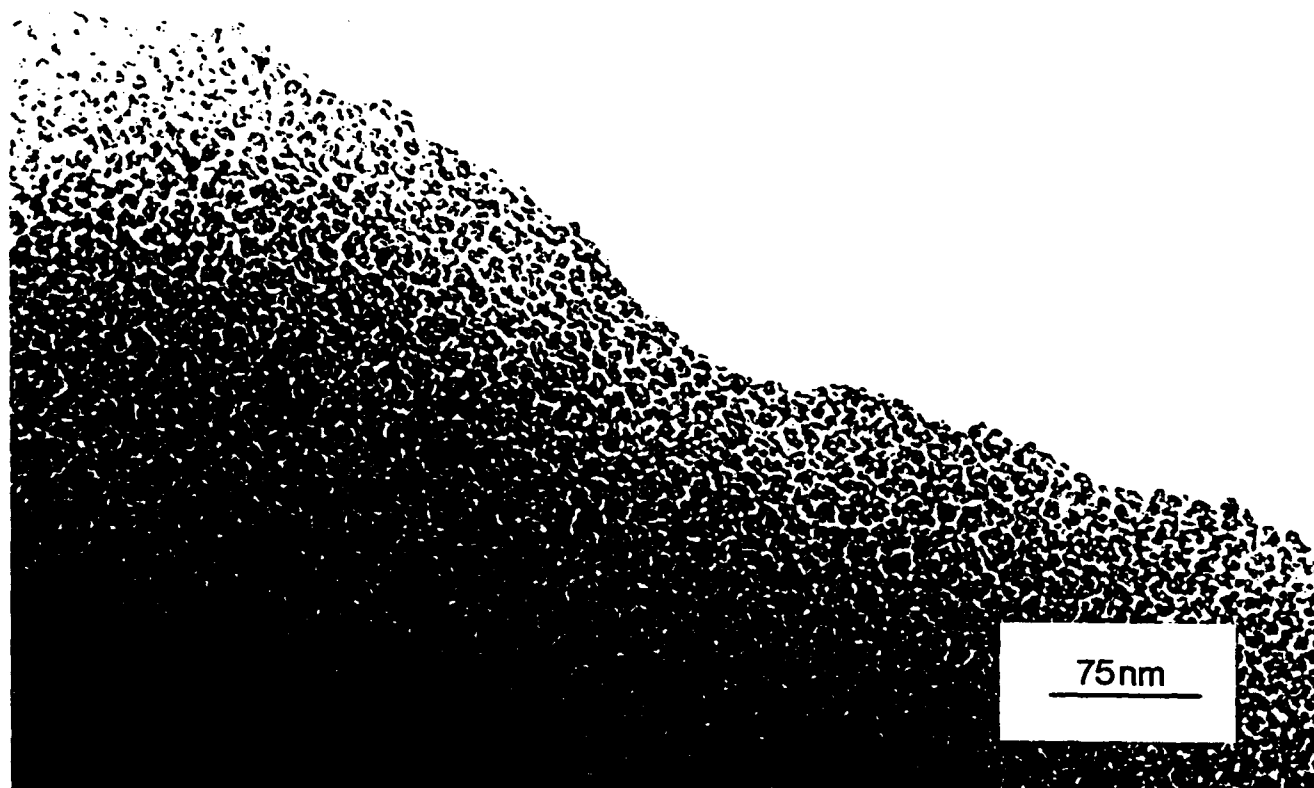
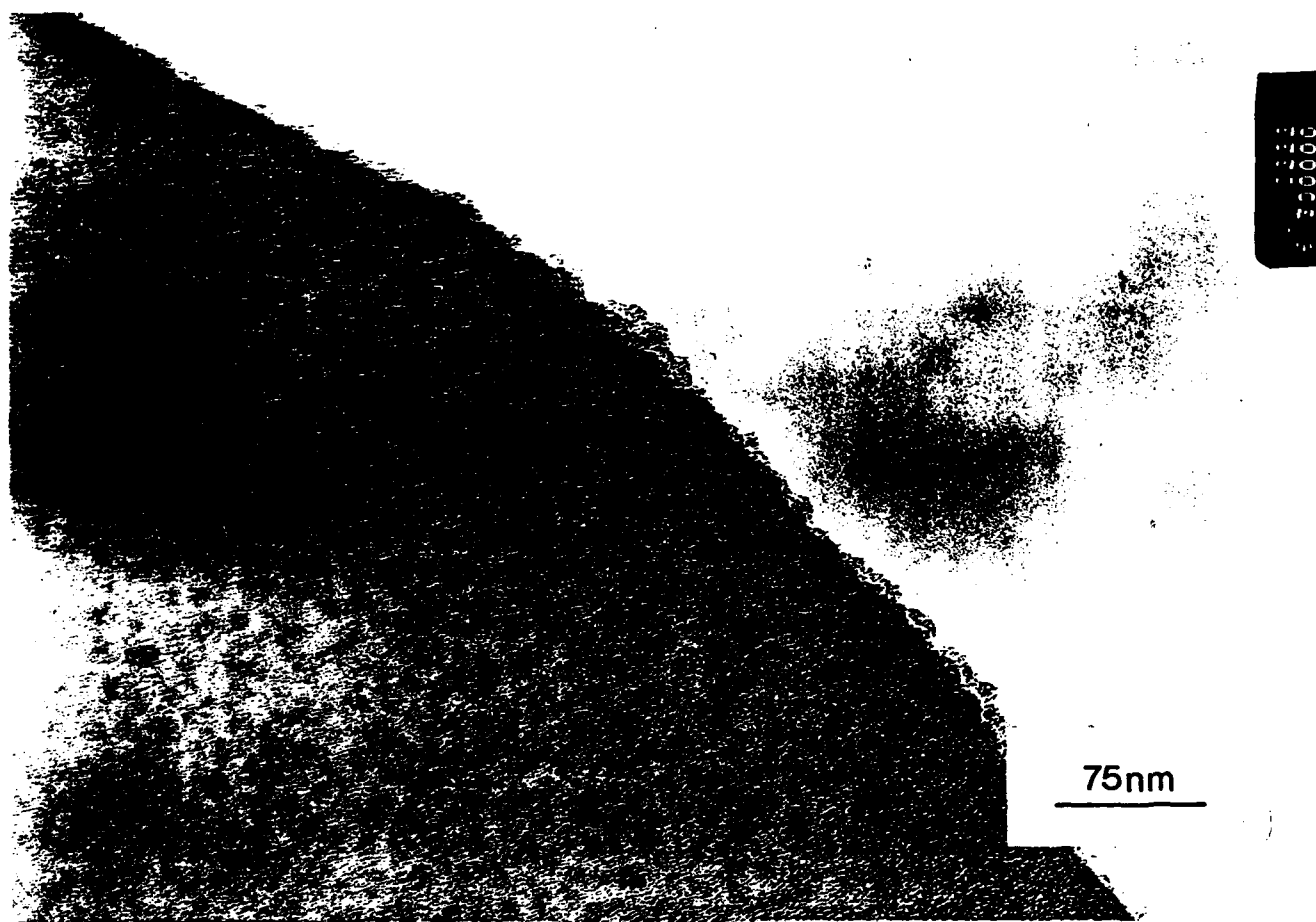




Fig 91



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