(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
25 May 2001 (25.05.2001)

PCT

(10) **International Publication Number**
WO 01/36705 A1

(51) **International Patent Classification**⁷: **C23C 16/40**, C09K 3/00

(21) **International Application Number:** PCT/US00/29299

(22) **International Filing Date:** 24 October 2000 (24.10.2000)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
09/440,235 15 November 1999 (15.11.1999) US
09/441,694 16 November 1999 (16.11.1999) US

(71) **Applicant: ADVANCED TECHNOLOGY MATERIALS, INC.** [US/US]; 7 Commerce Drive, Danbury, CT 06810 (US).

(72) **Inventors: HENDRIX, Bryan, C.**; 12 Peace Street, Danbury, CT 06810 (US). **BAUM, Thomas, H.**; 2 Handol Lane, New Fairfield, CT 06812 (US). **DESROCHERS, Debra**; 756 Federal Road, Brookfield, CT 06812 (US). **ROEDER, Jeffrey, F.**; 4 Longmeadow Hill, Brookfield, CT 06804 (US). **PAW, Witold**; 8 Mountain View Road, New Fairfield, CT 06812 (US).

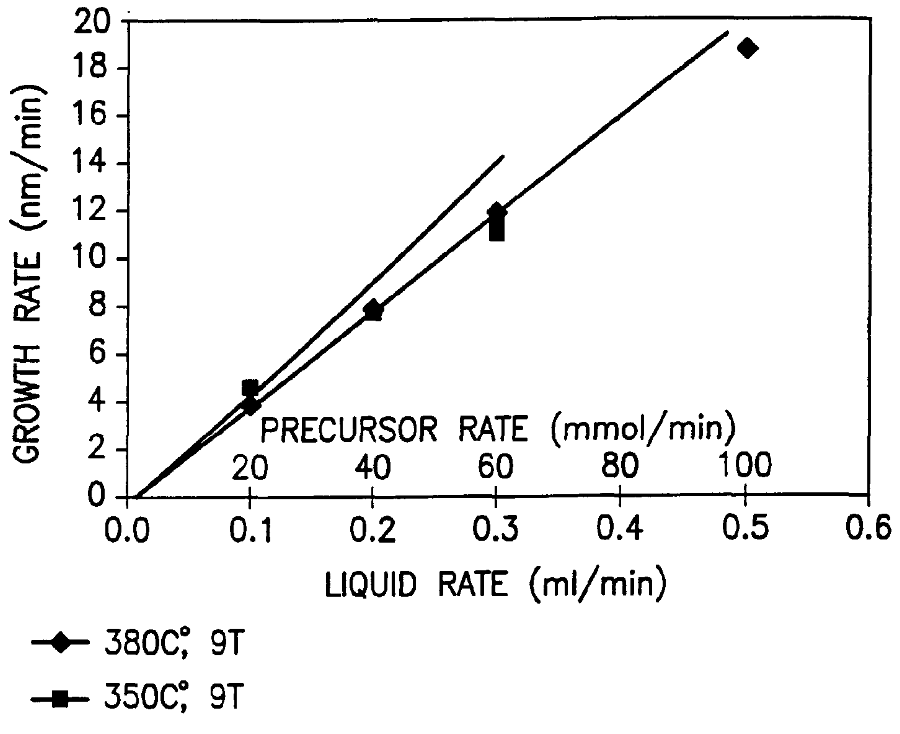
(74) **Agent: ZITZMANN, Oliver, A., M.**; Advanced Technology Materials, Inc., 7 Commerce Drive, Danbury, CT 06810 (US).

(81) **Designated States** *(national)*: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: LIQUID DELIVERY MOCVD OF SBT



(57) **Abstract:** A composition useful in MOCVD of SBT from SBT precursors, including a solvent. The solvent is (i) tetrahydrofuran, or (ii) a solution of toluene and a Lewis base in which toluene is present at a concentration of from about 75 % to about 98 % by volume, based on the total volume of toluene and the Lewis base. The composition is usefully employed for liquid delivery MOCVD of SBT films.

Published:
- *With international search report.*

LIQUID DELIVERY MOCVD OF SBT

DESCRIPTION

Field of the Invention

This invention relates to metalorganic chemical vapor deposition (MOCVD) of strontium bismuth tantalate, and in particular to solvent-based compositions and methods useful for precursor delivery in the MOCVD of such material.

Description of the Related Art

Liquid delivery MOCVD is the preferred method for depositing thin films of ferroelectric materials because of the ability to carefully control composition and deposit conformal films of high density. In such process a solution or suspension of precursors (metalorganic source reagents for the respective metal components of the product film material) is vaporized, preferably at high rate by "flash vaporization" techniques to produce a corresponding precursor vapor which may be mixed with carrier and/or additive gases (e.g., oxygen-containing gas, inert gases such as argon, helium, etc., co-reactive gases, diluents, etc.) to form a vapor mixture. The vapor mixture then is flowed to a deposition zone where the precursor mixture is contacted with a substrate at elevated temperature to effect deposition from the vapor phase onto the substrate of a desired material.

MOCVD of $SrBi_2Ta_2O_9$ (SBT) and related materials use precursors that are chemically compatible in solution for long periods of time and also have similar decomposition characteristics vis-à-vis one another in the MOCVD process. $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ (where thd stands for 2,2,7,7-tetramethyl-3,5-heptanedionato, LBA stands for a Lewis base adduct and O-i-Pr stands for isopropoxide) provide a preferred combination of precursors for such purpose. Precursors for deposition of SBT and other ferroelectric materials, and their use in liquid delivery MOCVD formation of high quality product films, are more fully described in United States Patent Application No. 08/960,915 filed October 30, 1997 in the names of Thomas H. Baum, et al., now issued as U.S. Patent 5,859,274, and United States Patent Application No. 08/976,087 filed November 20, 1997 in the names of Frank S. Hintermaier, et al.

The best previously known solvent system for this precursor suite (of $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$) consisted of alkanes and in particular a mixture of octane, decane, with an excess of the LBA of the strontium precursor, $Sr(thd)_2$. In particular, a ratio of 5 parts octane, 4 parts decane, and 1 part LBA was found to maintain the precursors in a stable condition and deliver them reliably to a flash vaporization equipment. Solvent compositions of such type are more fully described in United States Patent Application No. 08/975,372 filed November 20, 1997 in the names of Thomas H. Baum, et al., now issued as U.S. Patent No. 5,916,359.

However, the alkane-based solvents have limited solubility of the aforementioned SBT precursors, especially for the $Sr(thd)_2$, which only dissolves to about 0.2 M in a 5:4:1 mixture of octane:decane:pmdeta. This limited solubility characteristic of the solvent composition has disadvantages for liquid delivery vaporization and the subsequent deposition process. During vaporization, wherein the precursor solution typically is flowed through a liquid delivery tube to a heated surface, the molarity of the precursor solution must remain significantly below the solubility limit to prevent precipitation of solid metalorganic particles from the solution, which would otherwise occur as solvent boils off in the liquid delivery tube, and which would lead to clogging of the liquid delivery tube. In addition, low solution molarity requires the vaporization of more solvent in order to deliver the same amount of precursor to the process. This creates undue requirements for the supply of heat to the metalorganics in the vaporizer, since more heat must then be provided to volatilize the additional solvent that is present.

The deposition process itself also is adversely affected by low molarity solutions. By way of example, film growth rates were limited to 3-4 nanometers per minute (nm/min) in a prototype MOCVD reactor delivering a 0.30M solution at a rate of 0.2 ml/min. Growth rates should be 2-3 times higher than this level in order to meet the requirements of a "manufacturable process." In addition, limiting the rate of delivery of precursor to the substrate surface makes it more difficult to push the process into a surface kinetic-controlled growth regime where conformality to non-planar structures is improved, relative to film formation processes operating outside of such regime.

It would therefore be an advance in the art to provide a solvent medium for liquid delivery MOCVD of precursor compositions such as SBT, which overcome the aforementioned difficulties.

SUMMARY OF THE INVENTION

The present invention relates to a composition that is usefully employed for liquid delivery MOCVD applications, e.g., as a solvent medium for SBT and other ferroelectric precursors.

In one aspect, the invention relates to a composition useful in MOCVD of SBT from SBT precursors, such composition comprising a solvent selected from the group consisting of:

(a) tetrahydrofuran; and

(b) a solution of toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base;

wherein when the solvent is tetrahydrofuran, the composition comprises SBT precursors dissolved or suspended in the solvent.

In a further aspect, the invention relates to a solvent composition useful for liquid delivery MOCVD, comprising toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base.

Another aspect of the invention relates to a precursor composition useful for liquid delivery MOCVD, comprising (i) a solvent composition including toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about

98% by volume, based on the total volume of toluene and the Lewis base, and (ii) a precursor species dissolved or suspended in the solvent composition.

A still further aspect of the invention relates to a method of forming a material film on a substrate, comprising:

providing a precursor composition for at least one component of the material film;
volatilizing the precursor composition to yield a precursor vapor; and
contacting the precursor vapor with the substrate to deposit said at least one component of the material film thereon;

wherein the precursor composition comprises (i) a solvent composition including toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base, and (ii) a precursor species dissolved or suspended in the solvent composition.
The present invention in other aspects contemplates precursor compositions that are usefully employed for liquid delivery MOCVD applications, e.g., for SBT, doped SBT and other ferroelectric precursors, comprising SBT precursors dissolved in a solvent system containing tetrahydrofuran (THF). The solvent system may for example be constituted in major portion by THF, or it may be constituted solely by THF, or it may consist essentially of THF. In such precursor composition, $Sr(thd)_2(THF)_4$ is a preferred chemical species for the introduction of Sr.

The invention relates in another aspect to a precursor composition useful for liquid delivery MOCVD comprising SBT precursors dissolved in a solvent system comprising 90-99 parts by volume tetrahydrofuran and 1-10 parts by volume Lewis base ligand (LBA). In such composition, $Sr(thd)_2(LBA)_x$, wherein x is from 1 to 4, is a preferred chemical species for the introduction of Sr.

The invention relates in another aspect to a precursor composition useful for liquid delivery MOCVD, comprising SBT precursors and a dopant precursor, e.g., niobium beta-diketonate, dissolved in a solvent system including tetrahydrofuran. In such composition, $Sr(thd)_2(THF)_4$ is a preferred chemical species for the introduction of Sr.

The invention relates in a still further aspect to a precursor composition useful for liquid delivery MOCVD, comprising SBT precursors and a dopant precursor, e.g., niobium beta-diketonate, dissolved in a solvent system comprising 90-99 parts by volume tetrahydrofuran and 1-10 parts by volume LBA. In such composition, $Sr(thd)_2(LBA)_x$ wherein x is from 1 to 4, is a preferred chemical species for the introduction of Sr.

Another aspect of the invention relates to an SBT precursor composition comprising SBT precursors dissolved in a solvent medium including tetrahydrofuran, e.g., a solvent medium consisting essentially of tetrahydrofuran, with such SBT precursor composition having a boiling point at 1 atmosphere pressure of about 66°C. The SBT precursors of such composition desirably comprise $Sr(thd)_2(THF)_4$ as a preferred chemical species for the introduction of Sr due to its high solubility and low melting point.

Another aspect of the invention relates to an SBT precursor composition comprising SBT precursors and a dopant component, e.g., a dopant precursor, dissolved in a solvent medium containing tetrahydrofuran, having a boiling point at 1 atmosphere pressure of about 66°C. The SBT precursors of such composition desirably comprise $Sr(thd)_2(THF)_4$ as a preferred chemical species for the introduction of Sr due to its high solubility and low melting point.

A further aspect of the invention relates to a method of forming SBT material on a substrate, comprising:

providing a precursor composition for SBT;
volatilizing the precursor composition to yield a precursor vapor; and
contacting the precursor vapor with the substrate to deposit SBT thereon;
wherein the precursor composition comprises SBT precursors dissolved in a solvent medium containing tetrahydrofuran. The SBT precursors of such composition desirably comprise $Sr(thd)_2(THF)_4$ as a preferred chemical species for the introduction of Sr due to its high solubility and low melting point.

A further aspect of the invention relates to a method of forming doped SBT material on a substrate, comprising:

providing a precursor composition for doped SBT;
volatilizing the precursor composition to yield a precursor vapor; and
contacting the precursor vapor with a substrate to deposit doped SBT thereon.

In such method, the precursor composition advantageously comprises SBT precursors and a dopant precursor, e.g., niobium beta-diketonate, dissolved in a solvent medium containing tetrahydrofuran, wherein $Sr(thd)_2(THF)_4$ is a preferred chemical species for the introduction of Sr due to its low melting point and high solubility in THF.

A still further aspect of the invention relates to a method of forming SBT material on a substrate, comprising:

providing a precursor composition for SBT;

volatilizing the precursor composition to yield a precursor vapor; and

contacting the precursor vapor with a substrate to deposit SBT thereon, wherein the precursor composition comprises SBT precursors dissolved in a solvent system comprising 90-99 parts by volume tetrahydrofuran and 1-10 parts by volume LBA. In such composition, $Sr(thd)_2(LBA)_x$, wherein x is from 1 to 4, is a preferred chemical species for the introduction of Sr.

In another aspect, the invention relates to a method of forming an SBT film on a substrate, comprising liquid delivery MOCVD using a precursor composition comprising SBT precursors dissolved in a solvent medium containing tetrahydrofuran. In such composition, $Sr(thd)_2(THF)_4$ is a preferred chemical species for the introduction of Sr due to its low melting point and high solubility in THF.

In a further aspect, the invention relates to a method of forming a doped SBT film, e.g., niobium doped SBT, on a substrate, comprising liquid delivery MOCVD using a precursor composition comprising SBT precursors and a dopant precursor dissolved in a solvent medium containing tetrahydrofuran. In such composition, $Sr(thd)_2(THF)_4$

is a preferred chemical species for the introduction of Sr due to its low melting point and high solubility in THF.

A still further aspect of the invention relates to a method of forming an SBT film on a substrate, comprising liquid delivery MOCVD using a precursor composition comprising SBT precursors dissolved in a solvent system comprising tetrahydrofuran and a Lewis base ligand. In such composition, $Sr(thd)_2(LBA)_x$ wherein x is from 1 to 4, is a preferred chemical species for the introduction of Sr.

The aforementioned precursor compositions of the present invention provide preferred combinations of precursors that are chemically compatible in solution for extended periods of time and have similar decomposition characteristics vis-à-vis one another in the MOCVD process for deposition of SBT and other ferroelectric materials.

Other objects, features and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of the growth rate of an SBT film as a function of liquid delivery rate for 9 torr processes at 380°C and 350°C using 0.2M solution in 5:4:1 octane:decane:pmdeta.

Figure 2 is a graph of growth rate of an SBT film as a function of liquid delivery rate for 0.5M solution in 10:1 toluene:pmdeta at 380°C and 9 torr.

Figure 3 shows film incorporation efficiency of Sr, Bi and Ta, as a function of pressure (torr) at 380°C for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

Figure 4 is a graph of incorporation efficiency of Sr, Bi and Ta, as a function of temperature at 9 torr for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

Figure 5 is a graph of deposited film composition (Sr:2Ta, symbol "■;" Bi:2Ta, symbol "▲") as a function of pressure (torr) at 380°C for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

Figure 6 is a graph of deposited film composition (Sr:2Ta, symbol "■;" Bi:2Ta, symbol "▲") as a function of temperature at 9 torr for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

Figure 7 is a graph of linear pressure rise, in torr/100 milliliters of precursor solution, as a function of temperature, for a precursor solution of 5:4:1 octane:decane: pmdeta containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

Figure 8 is a graph of linear pressure rise, in torr/100 milliliters of precursor solution, as a function of temperature, for a precursor solution of 10:1 toluene: pmdeta solvent containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

Figure 9 is a graph of incorporation efficiencies of Sr, Bi and Ta, for (1) a precursor solution of 10:1 toluene: pmdeta solvent containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, (2) a precursor solution of 5:4:1 octane:decane: pmdeta containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, and (3) a precursor solution of tetrahydrofuran (THF), containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

Figure 10 shows film incorporation efficiency of Sr, Bi and Ta, for a precursor composition using tetrahydrofuran as a solvent and containing the precursors $Sr(thd)_2(THF)_4$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, and for a precursor solution of 5:4:1 octane:decane: pmdeta containing the precursors $Sr(thd)_2(pmdeta)$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3(pmdeta)$ and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

Figure 11 is a graph of linear and net pressure rises as a function of temperature for a precursor composition using tetrahydrofuran as a solvent and containing the precursors $Sr(thd)_2(THF)_4$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, with argon carrier gas.

Figure 12 is a graph of linear and net pressure rises as a function of temperature for a precursor composition using tetrahydrofuran as a solvent and containing the precursors $Sr(thd)_2(THF)_4$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, with helium carrier gas.

Figure 13 is a graph of repeatability in terms of linear and net pressure rises for precursor solutions of tetrahydrofuran solvent containing the precursors $Sr(thd)_2(THF)_4$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, in helium carrier gas.

Figure 14 is a graph of pressure rise as a function of volume of precursor flowed through a frit element for a precursor solution of tetrahydrofuran solvent containing the precursors $Sr(thd)_2(THF)_4$ (as a preferred chemical species for the introduction of Sr), $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

The disclosures of the following United States patents and patent applications are hereby incorporated herein by reference in their entireties:

- United States Patent Application No. 08/835,768 filed April 8, 1997 in the names of Thomas H. Baum, et al.;
- United States Patent Application No. 08/484,654 filed 7 June 1995 in the names of Robin A. Gardiner et al.;
- United States Patent Application No. 08/414,504 filed 31 March 1995 in the names of Robin A. Gardiner et al., now issued as U.S. Patent 5,820,664;

- United States Application No. 08/280,143 filed July 25, 1994, in the names of Peter S. Kirlin, et al.;
- United States Patent Application No. 07/927,134, filed August 7, 1992 in the same names;
- United States Patent Application No. 07/807,807, filed December 13, 1991 in the names of Peter S. Kirlin, et al., now issued as United States Patent No. 5,204,314;
- United States Application No. 08/181,800 filed January 15, 1994 in the names of Peter S. Kirlin, et al., and issued as United States Patent 5,453,494;
- United States Application No. 07/918,141 filed July 22, 1992 in the names of Peter S. Kirlin, et al., and issued January 18, 1994 as United States Patent 5,280,012;
- United States Application No. 07/615,303 filed November 19, 1990 in the names of Peter S. Kirlin, et al.;
- United States Application No. 07/581,631 filed September 12, 1990 in the names of Peter S. Kirlin, et al., and issued July 6, 1993 as U.S. Patent 5,225,561;
- United States Patent Application No. 07/549,389 filed July 6, 1990 in the names of Peter S. Kirlin, et al.;
- United States Patent Application No. 08/975,372 filed November 20, 1997 in the names of Thomas H. Baum, et al., now issued as U.S. Patent No. 5,916,359;

- United States Patent Application No. 08/960,915 filed October 30, 1997 in the names of Thomas H. Baum, et al., now issued as U.S. Patent 5,859,274; and
- United States Patent Application No. 08/976,087 filed November 20, 1997 in the names of Frank S. Hintermaier, et al.

The present invention in one aspect relates to the discovery of a toluene based solvent system, which in application to the MOCVD of SBT, has high solubility of all precursor components and no undesired chemical interactions.

For example, as applied to the MOCVD of SBT using the aforementioned preferred precursor combination of $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, it was found that the solubility of $Bi(thd)_3$ increased from 0.75M to 1M as the ratio of toluene:pmdeta (the Lewis base "pmdeta" is pentamethyldiethylenetriamine) changed from 25:1 to 10:1. This data is summarized in Table I below.

Table I. Solubility of SBT preferred precursors in various solvent systems.

	5:4:1 octane:decane:pmdeta	25:1 toluene:pmdeta	10:1 toluene:pmdeta
Boiling point	125-127°C	110.6°C	110.6°C
$Sr(thd)_2$-pmdeta	0.20M	1.00M	1.00M
$Bi(thd)_3$	0.50M	0.75M	1.00M
$Ta(O\text{-}i\text{-}Pr)_4(thd)$	1.00M	0.50M	0.50M

Vaporization of the SBT preferred precursors in the 10:1 toluene:pmdeta solution at 0.3 total solution molarity and 0.30ml/min gave vaporizer mean time to service (MTS) similar to the 5:4:1 octane:decane:pmdeta. The mean time to service is a measure of the extent of premature decomposition of the precursors in the vaporizer, the occurrence of side reactions in the vaporizer, and unwanted deposition of solids and viscous byproducts in the vaporizer. Thus, the "cleaner" the vaporization operation in the vaporizer zone, the longer will be the MTS for the system. It is highly desirable to achieve MTS values as high as possible (i.e., the longest possible time between maintenance events for the vaporizer), since this maximizes on-stream time and equipment utility, and minimizes operating costs of the liquid vaporization MOCVD system.

The above-tabulated results achieved by high toluene content solvent compositions for the MOCVD of SBT, viz., vaporization of the SBT preferred precursors in the 10:1 toluene:pmdeta solution at 0.3 total solution molarity and 0.30ml/min yielding vaporizer MTS values similar to the use of 5:4:1 octane:decane:pmdeta solvent compositions for the same preferred SBT precursors, indicates that there are no adverse affects from the solvent system change and that vaporizer MTS is being primarily controlled by the precursors themselves. Despite the lower boiling point of the toluene solvent, there was surprisingly and unexpectedly no evidence of problems with precipitation from solvent boil-off in the delivery tube was observed.

As an example of the use and benefits of toluene-enhanced solvent compositions of the present invention for MOCVD of SBT using the aforementioned preferred precursors of $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, a liquid delivery MOCVD SBT process was conducted using 10:1 toluene:pmdeta solvent at 0.3M total solution molarity and at 0.5M total solution molarity. It was found that the 0.5 M solution enabled growth rates to be achieved that were nearly double those obtained for the

0.3M solution, thereby evidencing that the process is limited by precursor delivery to the growth surface.

From corresponding experiments in 5:4:1 solvent compositions of octane:decane:pmdeta, it was demonstrated that increased precursor delivery increases the growth rate of the films in the mass-transport controlled regime, and increases both the growth rate and the conformality of films when altering the process from being limited by mass-transport kinetics to being limited by surface reaction kinetics.

It was also demonstrated that the higher molarity solutions in 10:1 toluene:pmdeta lead to higher delivery rates of precursors and higher growth rates.

The invention therefore contemplates a solvent composition that is unexpectedly superior for liquid delivery of precursors for SBT, such as the preferred $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ precursors, that is readily formulated and permits high delivery rates and high growth rates to be achieved which provide a "manufacturable process" for thin film deposition of SBT by liquid delivery MOCVD techniques.

The solvent composition of the invention comprises toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base.

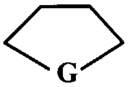
In application to the liquid delivery MOCVD of SBT films, toluene preferably is present at a concentration of from about 90% to about 97% by volume, based on the total volume of toluene and Lewis base. Such solvent composition may for example have a boiling point in the range of from about 109.5 to about 112.0°C. In a particular embodiment for liquid delivery MOCVD of SBT, the volumetric ratio of toluene to the Lewis base is about 10:1.

The solvent composition may comprise any suitable Lewis base, as for example a Lewis base comprising at least one of the following:

(a) amines and polyamines;

(b) N, S and O-containing aromatics;

(c) ligands of the formula:



wherein:

G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

(d) crown ethers;

(e) thioethers;

(f) ammonia and other nitrogenous species; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl, perfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

Preferred Lewis base species of such type include:

polyamines;
pyridines;
bipyridines;
phenylpyridines;
ammonia;
crown ethers; and
species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethylperfluoro-n-propyl, or vinyl;
R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;
R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;
n = 2, 3 ,4, 5, or 6; and
each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

Particularly preferred Lewis base species include tetraglyme, tetrahydrofuran, bipydridine, ammonia, pyridine, 3-phenylpyridine, 3-picoline, 18-crown-6 ethers, and amines/polyamines, e.g., pentamethyldiethylenetriamine (PMDETA), diethylenetriamine (DETA), tetraethylenepentaamine (TEPA) and hexamethyltetraethylenepentaamine (HMTEPA).

A precursor composition useful for liquid delivery MOCVD may comprise the aforementioned solvent composition and a precursor species dissolved or suspended in the solvent composition. Such precursor species may include a precursor for a metal of a ferroelectric material, e.g., a precursor for strontium, bismuth and/or tantalum. Specific precursor species include $Sr(thd)_2$-LBA, where LBA is a Lewis base adducting species, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$. The Lewis base adducting species may suitably be the same as the Lewis base of the solvent composition.

In a preferred aspect, the precursor species comprise $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, where LBA is a Lewis base adducting species that coordinatively complexes with $Sr(thd)_2$. Such a precursor composition may have a total solution molarity of from about 0.3 M to about 0.7 M.

The above-described precursor composition may be utilized in a liquid delivery MOCVD method of forming a material film on a substrate, comprising the steps of:

providing a precursor composition for at least one component of the material film;
volatilizing the precursor composition to yield a precursor vapor; and
contacting the precursor vapor with the substrate to deposit said at least one component of the material film thereon.

The Lewis base component of the solvent composition of the invention may comprise any suitable Lewis base species that is compatible with the precursors that are employed in the corresponding precursor composition (including the solvent composition and the solute precursor species, e.g., metalorganic compounds or complexes for the metal components of the film to be formed by MOCVD using such precursor composition). The Lewis base may include Lewis base species that are selected to form adducts or coordination complexes with one or more of the precursor species.

The solvent composition of the invention may be readily formulated by simple mixing at ambient (room temperature) conditions of the respective toluene and Lewis base components.

The relative proportions of toluene and the Lewis base in respect of one another may be any suitable proportion that produce a metal-containing film with the desired characteristics when the precursor(s) of interest are dissolved or suspended therein and the resultant precursor composition is utilized for liquid delivery MOCVD.

For utilization in the liquid delivery MOCVD of SBT and other ferroelectric materials, the solvent compositions of the invention suitably comprise toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base. As used in such context, of the Lewis base being a component of the solvent composition of the invention, the term "Lewis base" is intended to be broadly construed to include a single Lewis base species, as well as to encompass multiple Lewis base species as the Lewis base component of the solvent composition.

In the case of preferred precursor combination of $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, the solvent composition is desirably formulated so that the volumetric ratio of toluene to the Lewis base is about 10:1.

The solvent composition after its formulation may be mixed with the precursor components under gentle mixing, e.g., with a mechanical agitator, inert gas sparger, static mixer, or other mixer device or method, tò place the precursor components in solution or suspension in the solvent medium, and thereby form the precursor composition, as a source material for liquid delivery MOCVD.

The precursor composition comprising the solvent composition and the dissolved or suspended precursor species therein then can be disposed in a supply vessel or feed liquid reservoir of a liquid delivery MOCVD system for the formation of a material on a substrate in a CVD reactor at suitable process conditions. The process conditions will depend on the specific material being deposited on the substrate, the configuration and geometry of the reactor, the precursor composition employed, and the rate of film growth being effected. The process conditions may readily be determined by suitable empirical approaches without undue experimentation, to determine appropriate temperatures, pressures, flow rates and compositional character of process streams.

The liquid delivery MOCVD system may comprise a system of the type disclosed in U.S. Patent 5,204,314 issued April 20, 1993 to Peter S. Kirlin et al. and in U.S. Patent 5,536,323 issued July 16, 1996 to Peter S. Kirlin et al., which describe heated vaporization structures such as microporous disk elements. In use, liquid source reagent compositions are flowed onto the vaporization structure for flash vaporization. Vapor thereby is produced for transport to the deposition zone, e.g., a CVD reactor. The liquid delivery systems of these patents provide high efficiency generation of vapor from which films may be grown on substrates.

The precursor vapor then is transported to a chemical vapor deposition zone containing a substrate, e.g., a wafer provided on a heated susceptor. Upon contacting of the precursor vapor with the wafer, the metal components of the vapor are deposited on the wafer surface. The vapor may be delivered in the chemical vapor deposition chamber by a disperser such as a showerhead or nozzle, to provide a uniform flux of the vapor across the width of the wafer, to yield a correspondingly uniform thickness of deposited metal-containing film on the wafer. The process conditions (temperature, pressure, flow rate and composition of the vapor) may be suitably controlled to ensure an optimum process result for the MOCVD operation being conducted in the process system.

The liquid delivery process utilizing precursor compositions of the invention to form a product material on a substrate therefore includes the steps of:

providing precursor species for at least one of the components of the product film to be formed on the substrate and solubilizing or suspending same in a solvent composition according to the invention to form a precursor composition comprising such precursor species and the solvent composition;

vaporizing the precursor composition to form corresponding precursor vapor; and contacting the precursor vapor with a substrate to deposit the product material thereon.

The advantages of the invention in respect of the toluene-based solvent compositions include the following:

(1) the toluene based solvents of the invention have increased solubility for the metalorganic precursors that are preferred for the deposition of $SrBi_2Ta_2O_9$ ceramics and derivatives thereof;

(2) the increased solubility allows more robust vaporization, increasing the resistance of the solution to delivery tube clogging in the liquid delivery apparatus;

(3) the increased concentration of metalorganic precursors in the toluene based solvent allows for vaporization of the precursors with less heat load from evaporating solvent;

(4) the increased concentration of metalorganic precursor in the toluene based solvent increases the growth rate of the film leading to a more manufacturable process; and

(5) the increased concentration of metalorganic precursor in the toluene based solvent increases the conformality of the films to non-planar structures leading to better performance of the product microelectronic device, e.g., ferroelectric capacitor.

The present invention in another aspect is based on the discovery that a tetrahydrofuran solvent system or solvent systems comprising tetrahydrofuran, when used for the liquid delivery MOCVD of SBT, has high solubility of all precursor components and no undesired chemical interactions. Further, $Sr(thd)_2(THF)_4$ is a preferred chemical species for the introduction of Sr (as a component into the product film deposited on the substrate), in consequence of its high solubility in THF and its low melting point. These characteristics significantly aid the "flash vaporization" of the precursor and transport of the chemical mixture to the chemical vapor deposition chamber.

For example, as applied to the MOCVD of SBT using the aforementioned preferred precursor combination of $Sr(thd)_2$, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, it was found that the tetrahydrofuran coordinates to the $Sr(thd)_2$ component of the precursor composition, yielding a precursor composition comprising $Sr(thd)_2$-LBA, wherein LBA is THF, that is in the liquid phase at low temperature (where $Sr(thd)_2(THF)_4$ melts at temperatures >28°C).

Further, it is expected that tetrahydrofuran coordinates to the $Bi(thd)_3$ component to produce a $Bi(thd)_3\text{-}(LBA)_x$ species, wherein LBA is THF and x has a value of 1 to 4, consistent with the discovery that Lewis base ligands form adducts with $Bi(thd)_3$ as more fully described in copending U.S. Patent Application No. 09/224,614 filed December 31, 1998 in the names of Thomas H. Baum, et al., now allowed.

Vaporization of such SBT precursor composition, comprising SBT precursors dissolved in tetrahydrofuran, at 0.3 M total solution molarity and a flow rate of

0.30ml/min gave vaporizer mean time to service (MTS) similar to a corresponding precursor composition in 5:4:1 octane:decane:pmdeta (ratio by volume). The mean time to service is a measure of the extent of premature decomposition of the precursors in the vaporizer, the occurrence of side reactions in the vaporizer, and unwanted deposition of solids and viscous byproducts in the vaporizer. Thus, the "cleaner" the vaporization operation in the vaporizer zone, the longer will be the MTS for the system. It is highly desirable to achieve MTS values as high as possible (i.e., the longest possible time between maintenance events for the vaporizer), since this maximizes on-stream time and equipment utility, and minimizes operating costs of the liquid vaporization MOCVD system.

The above-noted results achieved by the tetrahydrofuran solvent compositions for the MOCVD of SBT, viz., vaporization of the aforementioned SBT precursors in tetrahydrofuran solution at 0.3 total solution molarity and 0.30ml/min yielding vaporizer MTS values greater than the MTS for use of 5:4:1 octane:decane:pmdeta solvent compositions for the same SBT precursors, indicating that there are positive effects from the solvent system change and that vaporizer MTS is being primarily controlled by the precursors identities and solvents utilized. Despite the lower boiling point of the tetrahydrofuran solvent, there was surprisingly and unexpectedly no evidence of problems with precipitation from solvent boil-off in the delivery tube. These effects were primarily correlated with $Sr(thd)_2(THF)_4$, due to its high solubility and low melting point, as the preferred chemical species for the introduction and vaporization of Sr.

In addition, significantly improved vaporizer maintenance times were obtained with the tetrahydrofuran precursor compositions of the invention when the carrier gas was changed from argon to helium, and the average pore size of the vaporizer element was increased from a nominal 40 micrometers to nominal 100 micrometers.

The tetrahydrofuran-based precursor compositions of the present invention may be usefully employed for MOCVD of SBT and doped SBT using the aforementioned preferred precursors of Sr(thd)$_2$, Bi(thd)$_3$ and Ta(O-i-Pr)$_4$(thd) at a total solution molarity in the range of from about 0.2 M to about 0.6 M.

The invention therefore contemplates a solvent composition that is unexpectedly superior for liquid delivery of precursors for SBT, such as the preferred Sr(thd)$_2$, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd) precursors, that is readily formulated and permits high delivery rates and high growth rates to be achieved which provide a "manufacturable process" for thin film deposition of SBT by liquid delivery MOCVD techniques.

The invention further contemplates a solvent composition for liquid delivery of precursors for doped SBT, such as the preferred Sr(thd)$_2$, Bi(thd)$_3$ and Ta(O-i-Pr)$_4$(thd) precursors as well as a dopant precursor, such as Nb(O-i-Pr)$_4$(thd), that is readily formulated and permits high delivery rates and high growth rates to be achieved which provide a "manufacturable process" for thin film deposition of doped SBT by liquid delivery MOCVD techniques.

In the precursor composition of the invention, the Sr and Bi components may be beta-diketonates, such as the aforementioned "thd" beta-diketonate ligand. In tetrahydrofuran solution, the tetrahydrofuran coordinatively complexes with the beta-diketonate compounds to form an adduct.

In the precursor composition of the invention, the Ta component and the dopant component, e.g., Nb, may be beta-diketonates, such as the aforementioned "thd" beta-diketonate ligand. In particular, the precursor composition may for example comprise $Ta(O\text{-}i\text{-}Pr)_4(thd)$ and $Nb(O\text{-}i\text{-}Pr)_4(thd)$, respectively.

The β-diketonate ligand in the respective precursor components may be of any suitable type. Illustrative species and their notational abbreviations include: acac = acetylacetonate, more specifically 2,4-pentane dionate; hfacac (or hfac) = hexafluoroacetylacetonate, more specifically 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; tfacac (or tfac) = trifluoroacetylacetonate, more specifically 1,1,1-trifluoro-2,4-pentanedionate; thd = tetramethylheptanedionate, and more specifically 2,2,6,6-tetramethyl-3,5-heptanedionate; fod = fluorodimethyloctanedionate, more specifically 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; tod = trimethyloctanedionate, more specifically 2,2,7-trimethyl-3,5-octanedionate; and hfod = heptafluoro-dimethyloctanedionate. The corresponding β-thioketonate ligands may also be used and are identified consistently with the foregoing β-diketonate ligand notation, by prefixation of “s” to the corresponding β-diketonate ligand, e.g., shfac, sthd, etc. Thus the ß-diketonate ligands employed in metal source complexes of the present invention may usefully include acac, thd, fod, hfod, tfacac, and hfacac, and their corresponding thio analogs. Preferred THF adducts of the invention include Bi tris (2,2,6,6-tetramethyl-3,5-heptanedionate) and Sr bis (2,2,6,6-tetramethyl-3,5-heptanedionate).

In the precursor composition of the present invention, the THF ligands stabilize the mononuclear form of the precursor, and satisfy the coordination requirements of the metal center, thereby increasing the solubility and the volatility of the resultant complexes. While THF does not bind strongly and will readily dissociate upon heating or under vacuum from the complex, when the SBT beta-diketonate precursors of the invention are utilized in a solution of THF for liquid delivery chemical vapor deposition, the excess THF used as solvent effectively shifts the equilibrium to favor the THF adducted species. Such equilibrium shift thereby limits the loss or liberation of THF from the complex, so that the complex remains storage stable in the liquid solution, remains in the mononuclear form, remains exceedingly soluble and remains a low melting species. However, $Sr(thd)_2(THF)_4$ is readily volatilized and decomposed under chemical vapor deposition conditions to incorporate Sr into the SBT films.

The preferred precursor composition of the present invention, $Sr(thd)_2(THF)_4$, $Bi(thd)_3$ and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ dissolved in tetrahydrofuran, provides a preferred combination of precursors that are chemically compatible in solution for long periods of time and also have similar decomposition characteristics vis-à-vis one another in the MOCVD process.

The use of tetrahydrofuran in accordance with the present invention overcomes the deficiencies of the prior art vaporization approach of chelating the metal β-diketonate with ligands containing many donor atoms, such as crown ethers or lariat polyethers, to fulfill the coordination sphere. Such prior art vaporization approach, while providing some improvement in stability relative to the metal β-diketonate per se, does not fully resolve the solubility and melting point depression issues achieved in the present invention. The precursor composition of the present invention overcomes these deficiencies by providing SBT beta-diketonate precursor complexes from which the THF ligands such as $Sr(thd)_2(THF)_4$, and can be readily adapted to liquid delivery chemical vapor deposition conditions.

The THF adducted complexes may be readily obtained by cooling of the THF solutions of the corresponding metal β-diketonate, e.g., of Bi and/or Sr. The resulting solid complexes recovered from the THF solution are crystalline solids that have unusually low melting points and high solubilities in THF at room temperature (25°C).

The compositions of the invention and hereafter claimed may selectively and alternatively comprise, consist or consist essentially of any of specific compounds, complexes, components, ingredients, materials and parts specifically described herein, and may selectively and alternatively exclude any specific compounds, complexes, components, ingredients, materials and parts that are not specifically identified herein as being encompassed by compositions of the invention.

Lewis bases that may be employed in accordance with the present invention to form Lewis base precursor adducts include any suitable Lewis base species, e.g., ethers, glymes, amines, polyamines, etc. Some illustrative polyamines and their abbreviations are follows:

deta = diethylenetriamine;

hmtera = hexamethyltetraethylenepentaamine;

tepa = tetraethylenepentaamine;

pmdeta = pentamethyldiethylenetriamine; and

tmeda = tetramethylethylenediamine.

The precursor compositions of the present invention may be utilized in a liquid delivery MOCVD method of forming a material film on a substrate, comprising the steps of: providing the precursor composition for the material film desired; volatilizing the precursor composition to yield a precursor vapor; and contacting the precursor vapor with the substrate to deposit the material film thereon.

The relative proportions of tetrahydrofuran and the SBT precursor species in respect of one another may be any suitable proportion that produces an SBT film with the desired characteristics when the precursor(s) of interest are dissolved therein and the resultant precursor composition is utilized for liquid delivery MOCVD.

The solvent composition after its formulation may be mixed with the precursor components under gentle mixing, e.g., with a mechanical agitator, inert gas sparger, static mixer, or other mixer device or method, to place the precursor components in solution in the solvent medium, and thereby form the precursor composition, as a source material for liquid delivery MOCVD.

The precursor composition comprising the tetrahydrofuran and the dissolved precursor species therein then can be disposed in a supply vessel or feed liquid reservoir of a liquid delivery MOCVD system for the formation of a material on a substrate in a CVD reactor at suitable process conditions. The process conditions will depend on the specific material being deposited on the substrate, the configuration and geometry of the reactor, the precursor composition employed, and the rate of film growth being effected. The process conditions may readily be determined by suitable empirical approaches without undue experimentation, to determine appropriate temperatures, pressures, flow rates and compositional character of process streams.

The liquid delivery MOCVD system may comprise a system of the type disclosed in U.S. Patent 5,204,314 issued April 20, 1993 to Peter S. Kirlin et al. and in U.S. Patent 5,536,323 issued July 16, 1996 to Peter S. Kirlin et al., which describe heated vaporization structures such as microporous disk elements. In use, liquid source reagent compositions are flowed onto the vaporization structure for flash vaporization. Vapor thereby is produced for transport to the deposition zone, e.g., a CVD reactor. The liquid delivery systems of these patents provide high efficiency generation of vapor from which films may be grown on substrates.

The precursor vapor then is transported to a chemical vapor deposition zone containing a substrate, e.g., a wafer provided on a heated susceptor. Upon contacting of the precursor vapor with the wafer, the metal components of the vapor are deposited on the wafer surface. The vapor may be delivered in the chemical vapor deposition chamber by a disperser such as a showerhead or nozzle, to provide a uniform flux of the vapor across the width of the wafer, to yield a correspondingly uniform thickness of deposited metal-containing film on the wafer. The process conditions (temperature, pressure, flow rate and composition of the vapor) may be suitably controlled to ensure an optimum process result for the MOCVD operation being conducted in the process system.

The liquid delivery process utilizing precursor compositions of the invention to form an SBT material on a substrate therefore includes the steps of:

providing precursor species for the product film to be formed on the substrate and solubilizing same in a solvent comprising tetrahydrofuran according to the invention to form a precursor composition comprising such precursor species and the solvent;

vaporizing the precursor composition to form corresponding precursor vapor; and

contacting the precursor vapor with a substrate to deposit the product material thereon.

The advantages of the invention in respect of the use of tetrahydrofuran as a solvent include the following:

(1) the tetrahydrofuran solvent of the invention has increased solubility for the metalorganic precursors that are preferred for the deposition of $SrBi_2Ta_2O_9$ ceramics and derivatives thereof;

(2) the increased solubility allows more robust vaporization, increasing the resistance of the solution to delivery tube clogging within the liquid delivery apparatus;

(3) the increased concentration of metalorganic precursors in the tetrahydrofuran solvent allows for vaporization of the precursors with less heat load from evaporating solvent;

(4) the increased concentration of metalorganic precursor in the tetrahydrofuran solvent increases the growth rate of the film leading to a more manufacturable process; and

(5) the increased concentration of metalorganic precursor in the tetrahydrofuran solvent increases the conformality of the films to non-planar structures leading to better performance of the product microelectronic device, e.g., ferroelectric capacitor.

The features and advantages of the invention are more fully shown with reference to the following non-limiting examples.

EXAMPLE 1

Experiments were performed using (1) a baseline 5:4:1 solvent system with a total precursor molarity of 0.20, (2) a 10:1 toluene:pmdeta solvent with the concentrations of each metalorganic fixed at the same values with a total solution molarity of 0.3M, and (3) a 10:1 toluene:pmdeta solvent with the concentrations of each metalorganic fixed at the same values with a total precursor molarity of 0.5.

The liquid delivery system used in these experiments was a Sparta^{TM} 450 liquid delivery system (commercially available from Advanced Technology Materials, Inc., Danbury, CT) equipped with a ½" vaporizer. The liquid delivery system was attached to a 5" diameter quartz tube reactor as the MOCVD deposition chamber, and such reactor was equipped with temperature controls for independent control of reactor wall temperature and substrate temperature. For films grown in the mass transport limited regime, this reactor enabled growth rates about 3 times greater than the prototype MOCVD reactor mentioned in the Background of the Invention section hereof.

Experiments using 0.2M solution in 5:4:1 solvent showed (1) that the film growth rate was controlled by the rate of delivery of precursor to the surface and (2) that faster precursor delivery to the surface increased conformality.

Figure 1 shows the growth rate of SBT films as a function of liquid delivery rate for 9 torr processes at 380°C and 350°C using 0.2M solution in 5:4:1 octane:decane:pmdeta. Lines indicating a linear proportional increase in growth rate are shown for comparison to the measured increase in growth rate.

Two different growth temperatures were used at a process pressure of 9 torr and 76% O_2. At 380°C, the growth rate increases linearly proportionally with the liquid delivery rate up to 60 mmol/min. The drop-off at 0.5 ml/min is attributed to either the onset of surface reaction limitation or a limitation in the vaporizer's ability to completely vaporize the liquid. At 380°C, the conformality of 1 μm wide by 1μm deep trenches was 20-30% independent of growth rate.

At 350°C, the growth rate is less than linearly proportional to the liquid delivery rate, but still increases by more than a factor of 2 for a factor of 3 increase in precursor delivery rate. Also, the conformality of the same 1 X 1 μm trench structures was 30% at 20 mmol/min and 70-80% at 60 mmol/min. This indicates that at the lower temperature, the growth rate becomes dependent upon the surface reaction kinetics in addition to the rate of precursor delivery to the surface, and that as the delivery rate increases, the conformality improves. The data show that there was no growth rate penalty incurred in going to the lower temperature process.

Next, experiments were performed with 0.3M and 0.5M solutions in 10:1 toluene:pmdeta. Figure 2 is a graph of growth rate as a function of precursor liquid delivery rate for 0.5M solution in 10:1 toluene:pmdeta at 380°C and 9 torr. At a liquid delivery rate of 0.1 ml/min, the delivery of precursors increased by a factor of 2.5 over the 0.2M solution (from 20 mmol/min to 50 mmol/min), and the growth rate increased by a factor of about 3. The growth rate was no longer proportional to liquid delivery rate at this temperature. Conformality was not tested under these conditions, and it therefore is difficult to determine whether this deviation from linear proportionality reflects movement into the surface reaction controlled growth regime or simply a decrease in vaporization efficiency from the higher heat load of evaporating the precursors at a higher rate. In either case, it is clear that precursor was delivered to the substrate surface at a higher rate with the increase in solution concentration. There was no growth rate penalty incurred in going to the lower temperature process for the higher concentration (molarity) solution.

EXAMPLE 2

A 10:1 toluene: pmdeta solvent composition was made up and utilized for dissolution therein of SBT precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ wherein the LBA was pmdeta.

The solution had a total molarity of 0.3 M, comprising 0.128 M strontium, 0.099 M bismuth and 0.073 M tantalum.

A liquid delivery MOCVD system of the type described in Example 1 was employed to deposit films of SBT, at a precursor delivery rate of 0.10 milliliters per minute (ml/min), and oxygen was introduced as a carrier gas to the vaporizer so that the precursor vapor mixture (precursor vapor + carrier gas) contained 76% O_2 by volume, and an SBT film was deposited on a substrate in the MOCVD reactor.

The data generated in the runs are shown in the graphs of Figures 3-6.

Figure 3 shows film incorporation efficiency of Sr, Bi and Ta, as a function of pressure (torr) at 380°C for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$. Figure 4 is a corresponding plot of incorporation efficiency of Sr, Bi and Ta, as a function of temperature at 9 torr for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

Figure 5 is a graph of deposited film composition (Sr:2Ta, symbol "■;" Bi:2Ta, symbol "▲") as a function of pressure (torr) at 380°C for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$. Figure 6 is a corresponding graph of deposited film composition (Sr:2Ta, symbol "■;" Bi:2Ta, symbol "▲") as a function of temperature at 9 torr for precursor solutions of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd).

EXAMPLE 3

A precursor solution of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd) was comparatively tested against a corresponding precursor solution of 5:4:1 octane:decane: pmdeta using a vaporizer of the type described in Example 1, with a 300 standard cubic centimeters per minute flow rate of argon carrier gas, a precursor solution liquid flow rate of 0.3 milliliters per minute, and a porous frit vaporizer element having 40 micrometers diameter pores. Linear pressure rise, in torr/100 milliliters of precursor solution, and pressure recovery, in torr, were determined for the respective precursor solutions, yielding the graphs of Figures 7 and 8.

EXAMPLE 4

A precursor solution of 10:1 toluene: pmdeta solvent containing the precursors Sr(thd)$_2$-LBA, Bi(thd)$_3$, and Ta(O-i-Pr)$_4$(thd) was comparatively tested against a corresponding precursor solution of 5:4:1 octane:decane: pmdeta and a corresponding precursor solution of tetrahydrofuran (THF), using a vaporizer and MOCVD reactor of the type described in Example 1. The ratio of metals in the solution was 43:33:24 Sr:Bi:Ta; the films were deposited in 9 torr of process gas containing 76% O$_2$.

The incorporation efficiency of Sr, Bi and Ta were determined. Efficiency is the fraction of the precursor delivered to the process that is actually incorporated into the product SBT film.

Efficiencies for the above precursor solutions are shown in Figure 9. These data show that the incorporation efficiency of strontium in the toluene-based solvent composition of the invention was significantly higher than that achieved by either of the other two solvent compositions and that the toluene-based composition concurrently yielded high bismuth and tantalum film incorporation efficiencies.

EXAMPLE 5

Experiments were performed using (1) a baseline 5:4:1 solvent system with a total precursor molarity of 0.20, and (2) a tetrahydrofuran solvent with the concentrations of each metalorganic fixed at the same values with a total solution molarity of 0.3M. The ratios of the different precursors were the same in both systems.

The liquid delivery system used in these experiments was a Sparta^{TM} 450 liquid delivery system (commercially available from Advanced Technology Materials, Inc., Danbury, CT) equipped with a ½" vaporizer. The liquid delivery system was attached to a 5" diameter quartz tube reactor as the MOCVD deposition chamber, and such reactor was equipped with temperature controls for independent control of reactor wall temperature and substrate temperature. For films grown in the mass transport limited regime, this reactor enabled growth rates about 3 times greater than the prototype MOCVD reactor mentioned in the Background of the Invention section hereof.

Experiments using 0.2M solution in 5:4:1 solvent showed (1) that the film growth rate was controlled by the rate of delivery of precursor to the surface and (2) that faster precursor delivery to the surface increased conformality.

The growth rate of SBT films as a function of liquid delivery rate was evaluated for 9 torr processes at 380°C and 350°C using 0.2M solution in 5:4:1 octane:decane:pmdeta.

Two different growth temperatures were used at a process pressure of 9 torr and 76% O_2. At 380°C, the growth rate increased linearly proportionally with the liquid delivery rate up to 60 mmol/min. A drop-off at 0.5 ml/min was attributed to either the onset of surface reaction limitation or a limitation in the vaporizer's ability to completely vaporize the liquid. At 380°C, the conformality of 1 μm wide by 1μm deep trenches was 20-30% independent of growth rate.

At 350°C, the growth rate was less than linearly proportional to the liquid delivery rate, but still increased by more than a factor of 2 for a factor of 3 increase in precursor delivery rate. Also, the conformality of the same 1 X 1 μm trench structures was 30% at 20 mmol/min and 70-80% at 60 mmol/min. This indicates that at the lower temperature, the growth rate becomes dependent upon the surface reaction kinetics in addition to the rate of precursor delivery to the surface, and that as the delivery rate increases, the conformality improves. The data show that there was no growth rate penalty incurred in going to the lower temperature process.

Next, a film was grown with a 0.3M solution in THF. The deposition temperature was 380°C, pressure was 9 torr, the gas was 76% O_2, the liquid delivery rate was 0.1 ml/min, and the deposition time was 40 minutes. The film was 290 nm thick and had a composition of $Sr_{0.6}Bi_{2.6}Ta_2O_9$.

Figure 10 compares the efficiencies of the individual precursors in this run to those in an equivalent run in the 5:4:1 octane:decane:pmdeta solvent. (Efficiency is defined as the fraction of the precursor delivered to the process that is actually incorporated into the film.) The comparable efficiencies evidence the behavior of the process behaves as being similar to the process with the 5:4:1 octane:decane:pmdeta solvent.

EXAMPLE 6

A tetrahydrofuran solution of $Sr(thd)_2(THF)_4$, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ was employed to test vaporizer performance in accordance with the invention, using a liquid delivery MOCVD system of the type described in connection with Example 5, equipped with a 3/4" VAPORSOURCE® vaporizer. In this system, argon was employed as a carrier gas, at a flow rate of 300 sccm, a liquid flow rate of 0.3 milliliters per minute was employed, with a total volume of precursor per run, of 50 milliliters. The vaporization elements in the system were stainless steel frits having a pore size of 40 micrometers.

Each experiment was performed by monitoring the pressure above the porous frit element of the vaporizer as a function of time while maintaining the pressure downstream of the frit at 9 Torr using a throttle valve. The pressure above the frit increases as its pores clog with unevaporated precursor residue. Starting with a clean frit element, the rate of pressure rise decreases with time to some "pseudo-steady-state," defined here as the linear pressure rise. After 50 ml of solution have been delivered, the liquid flow is stopped and the pressure above the frit recovers to some steady-state value indicative of the total amount of decomposed precursor in the frit. The pressure rise from the beginning of the run to this final steady-state condition is defined as the net pressure rise.

Large net pressure rise is indicative of decomposed precursor building up in the frit with time. A high rate of linear pressure rise can be the result of unevaporated precursor buildup if it is accompanied by a low pressure recovery. However, if a high rate of linear pressure rise is accompanied by a low pressure recovery, then it is probably indicative of precursor decomposing in the frit before it can be evaporated, which means the vaporization temperature is higher than optimum.

Linear and net pressure rise was determined as a function of temperature during the runs, generating the data shown in Figure 11.

Figure 11 shows a plot of ΔP_{linear} and ΔP_{net} as a function of temperature for each of the three runs. Both of these pressure parameters were higher at 190°C. ΔP_{linear} is the most relevant for predicting vaporizer MTS because it describes long term behavior under steady state conditions, as would be used in a manufacturing environment. Higher pressure rise, along with pressure recovery, indicate that 190°C may be too low for optimal vaporization of this precursor composition. Over 210-230°C, ΔP_{net} does not vary much, although the lower value, 3.4 Torr, is at 230°C. Delta P_{linear}, however, is minimized at 210°C (3.4 T/100mL). Under the conditions of this temperature scan, the optimal vaporization was at 210°C, since ΔP_{linear} appears significantly lower there than at 230°C.

Additional experimentation was carried out with the goal of achieving higher vaporizer on-stream MTS, and for this purpose a temperature scan experiment was designed using a combination of parameters expected to yield higher MTS. Larger frit pore size (100μm) and a different carrier gas (He) were introduced. A temperature scan was completed under these conditions, again with 20°C increments, 50mL total liquid volume, and 300sccm carrier gas flow rate. A liquid flow rate of 0.2mL/min was used, consistent with the baseline 5:4:1 octane:decane:pmdeta solvent liquid delivery MOCVD process; the higher solubilities of the precursors in the THF solvent can be used to improve growth rate without increasing liquid flow rate to higher levels.

A summary of P_{linear} and ΔP_{net} for the second temperature scan is shown in Figure 12, which shows linear and net pressure rises as a function of temperature for off-line vaporizer experiments completed with THF solvent system, helium carrier gas at 300sccm, 100μm stainless steel frits, a 0.2mL/min liquid flow rate, and a 50mL total precursor volume per run. At 210°C, decomposition was observed with ΔP_{linear} of 0.8T/100mL and ΔP_{net} of 1.1 Torr. At 170°C, recovery was observed with pressure rises of ΔP_{linear} = 0.8 Torr/100mL and ΔP_{net} = 1.9 Torr. At the midpoint, 190°C, a pressure rise of ΔP_{linear} = 0.2T/100mL and ΔP_{net} = 0.5 Torr were observed, and decomposition was noted as the pressure rise mechanism.

The 190°C condition was replicated to determine repeatability. The first of three runs showed decomposition, the second and third runs at this condition exhibited small pressure recoveries. The ΔP_{linear} was remarkably consistent over the three runs: 0.1-0.2 torr/100mL. The ΔP_{linear} was corrected in one of the runs (run 77) to account for a carrier gas control problem during the second half of the run; this value was measured over 35mL instead of 50mL. Both this run and the other (50mL) runs were extrapolated to 100mL. The ΔP_{net} was unaffected.

The ΔP_{net} varied over 0.1-1.15 Torr. The repeatability range for ΔP_{net} of this solvent system at this condition measured over 3 runs (0.65 Torr) is similar to that of the octane/decane/pmdeta (5:4:1) solvent system, measured over 6 runs (0.7 Torr).

Figure 13 shows the repeatability for these runs in terms of linear and net pressure rises of 3 runs done with THF solvent system, using 100μm stainless steel frits, at a 190°C temperature, with a 300sccm flow of helium carrier gas, and a 0.2mL/min liquid flow rate, providing a total volume of 50mL total precursor per run.

Figure 14 shows the pressure rise as a function of volume of precursor flowed through one 100μm stainless steel frit in such system. The THF precursor was flowed in three increments of 100mL at a temperature of 190°C, a carrier gas flow rate of helium carrier gas of 300sccm, and a liquid flow rate of 0.2mL/min for the precursor.

The foregoing results show that significantly improved vaporizer maintenance times were achieved with the tetrahydrofuran-based SBT precursor solutions when using helium as a carrier gas rather than argon, and when using a larger pore size in the porous vaporization element on which the precursor solution is flash vaporized for transport to the CVD reactor. Specifically, the average pore size of the vaporizer element (measured by standard porosimetry techniques) at a value of about 100 micrometers was found to provide significantly better performance than a corresponding vaporizer element having an average pore diameter of about 40 micrometers.

The foregoing results are consistent with the preferred average pore size (diameter) of the vaporization element being in the range of from about 50 to about 200 microns, more preferably in the range of from about 60 to about 120 micrometers, and most preferably in the range of from about 80 to about 110 micrometers. Within these diameter ranges, the viscosity and surface tension (free energy) of the precursor solution are efficiently balanced with the surface area and the capillarity of the porous vaporization element, so that the precursor liquid is quickly thinned and "flash" vaporized as it is applied to the porous vaporization element.

****

While the invention has been illustratively described herein with reference to various embodiments and disclosed features, it will be appreciated that the invention is not thus limited, but rather extends to and encompasses numerous variations, modifications and other embodiments. Accordingly, the invention is intended to be broadly construed and interpreted as including all such variations, modifications and other embodiments within the spirit and scope thereof, as hereinafter claimed.

THE CLAIMS

1. A composition useful in MOCVD of SBT from SBT precursors, said composition comprising a solvent selected from the group consisting of:

   (c) tetrahydrofuran; and

   (d) a solution of toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base;

   wherein when said solvent is tetrahydrofuran, said composition comprises SBT precursors dissolved or suspended in said solvent.

2. A solvent composition useful for liquid delivery MOCVD, comprising toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base.

3. The solvent composition of claim 2, wherein toluene is present at a concentration of from about 90% to about 97% by volume, based on the total volume of toluene and Lewis base.

4. The solvent composition of claim 2, having a boiling point in the range of from about 109.5 to about 112.0°C.

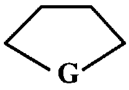
5. The solvent composition of claim 2, wherein the volumetric ratio of toluene to the Lewis base is about 10:1.

6. The solvent composition of claim 2, wherein the Lewis base is selected from the group consisting of:

(a) amines and polyamines;

(b) N, S and O-containing aromatics;

(c) compounds of the formula:



wherein:

G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

(d) crown ethers;

(e) thioethers;

(f) ammonia and other nitrogenous species; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl, perfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

7. The solvent composition of claim 2, wherein the Lewis base is selected from the group consisting of:

   (a) polyamines;
   (b) pyridines;
   (c) bipyridines;
   (d) phenylpyridines;
   (e) ammonia;
   (f) crown ethers; and
   (g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethylperfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

8. The solvent composition of claim 2, wherein the Lewis base is selected from the group consisting of: tetraglyme, tetrahydrofuran, bipydridine, ammonia, pyridine, 3-phenylpyridine, 3-picoline, 18-crown-6 ethers, and amines/polyamines.

9. The solvent composition of claim 2, wherein the Lewis base is selected from the group consisting of: pentamethyldiethylenetriamine (PMDETA),

diethylenetriamine (DETA), tetraethylenepentaamine (TEPA) and hexamethyltetraethylenepentaamine (HMTEPA).

10. A precursor composition useful for liquid delivery MOCVD, comprising (i) a solvent composition including toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base, and (ii) a precursor species dissolved or suspended in the solvent composition.

11. The precursor composition of claim 10, wherein toluene is present at a concentration of from about 90% to about 97% by volume, based on the total volume of toluene and Lewis base.

12. The precursor composition of claim 10, having a boiling point in the range of from about 109.5 to about 112.0°C.

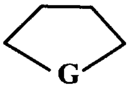
13. The precursor composition of claim 10, wherein the volumetric ratio of toluene to the Lewis base is about 10:1.

14. The precursor composition of claim 10, wherein the Lewis base is selected from the group consisting of:

(a) amines and polyamines;

(b) N, S and O-containing aromatics;

(c) ligands of the formula:



wherein:

G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

(d) crown ethers;

(e) thioethers;

(f) ammonia and other nitrogenous species; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl, perfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

15. The precursor composition of claim 10, wherein the Lewis base is selected from the group consisting of:

(a) polyamines;

(b) pyridines;

(c) bipyridines;

(d) phenylpyridines;

(e) ammonia;

(f) crown ethers; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethylperfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

16. The precursor composition of claim 10, wherein the Lewis base is selected from the group consisting of: tetraglyme, tetrahydrofuran, bipydridine, ammonia, pyridine, 3-phenylpyridine, 3-picoline, 18-crown-6 ethers, and amines/polyamines.

17. The precursor composition of claim 10, wherein the Lewis base is selected from the group consisting of: pentamethyldiethylenetriamine (PMDETA), diethylenetriamine (DETA), tetraethylenepentaamine (TEPA) and hexamethyltetraethylenepentaamine (HMTEPA).

18. The precursor composition of claim 10, wherein the precursor species comprises a precursor for a metal of a ferroelectric material.

19. The precursor composition of claim 10, wherein the precursor species comprises a precursor for strontium.

20. The precursor composition of claim 10, wherein the precursor species comprises a precursor for bismuth.

21. The precursor composition of claim 10, wherein the precursor species comprises a precursor for tantalum.

22. The precursor composition of claim 10, wherein the precursor species comprises $Sr(thd)_2$-LBA, where LBA is a Lewis base adducting species.

23. The precursor composition of claim 22, wherein the Lewis base adducting species is the same as the Lewis base of the solvent composition.

24. The precursor composition of claim 10, wherein the precursor species comprises $Bi(thd)_3$.

25. The precursor composition of claim 10, wherein the precursor species comprises $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

26. The precursor composition of claim 10, wherein the precursor species comprises $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, where LBA is a Lewis base adducting species that coordinatively complexes with $Sr(thd)_2$.

27. The precursor composition of claim 26, wherein the total solution molarity is from about 0.3 M to about 0.7 M.

28. A method of forming a material film on a substrate, comprising:

(a) providing a precursor composition for at least one component of the material film;

(b) volatilizing the precursor composition to yield a precursor vapor; and

(c) contacting the precursor vapor with the substrate to deposit said at least one component of the material film thereon;

wherein the precursor composition comprises (i) a solvent composition including toluene and a Lewis base, wherein toluene is present at a concentration of from about 75% to about 98% by volume, based on the total volume of toluene and the Lewis base, and (ii) a precursor species dissolved or suspended in the solvent composition.

29. The method of claim 28, wherein toluene is present in the precursor composition at a concentration of from about 90% to about 97% by volume, based on the total volume of toluene and Lewis base.

30. The method of claim 28, wherein the solvent composition has a boiling point in the range of from about 109.5 to about 112.0°C.

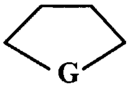
31. The method of claim 28, wherein the solvent composition has a volumetric ratio of toluene to the Lewis base is about 10:1.

32. The method of claim 28, wherein the Lewis base is selected from the group consisting of:

(a) amines and polyamines;

(b) N, S and O-containing aromatics;

(c) ligands of the formula:



wherein:

G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

(d) crown ethers;

(e) thioethers;

(f) ammonia and other nitrogenous species; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl, perfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

33. The method of claim 28, wherein the Lewis base is selected from the group consisting of:

(a) polyamines;

(b) pyridines;

(c) bipyridines;

(d) phenylpyridines;

(e) ammonia;

(f) crown ethers; and

(g) species of the formula: $R^0O(C(R^1)_2C(R^2)_2O)_nR^0$ wherein:

R^0 = H, methyl, ethyl, n-propyl, cyanato, perfluoroethylperfluoro-n-propyl, or vinyl;

R^1 = H, F, or a sterically acceptable hydrocarbyl substituent;

R^2 = H, F, or a sterically acceptable hydrocarbyl substituent;

n = 2, 3 ,4, 5, or 6; and

each R^0, R^1, and R^2 may be the same as or different from the other R^0, R^1, and R^2, respectively.

34. The method of claim 28, wherein the Lewis base is selected from the group consisting of: tetraglyme, tetrahydrofuran, bipydridine, ammonia, pyridine, 3-phenylpyridine, 3-picoline, 18-crown-6 ethers, and amines/polyamines.

35. The method of claim 28, wherein the Lewis base is selected from the group consisting of: pentamethyldiethylenetriamine (PMDETA), diethylenetriamine (DETA), tetraethylenepentaamine (TEPA) and hexamethyltetraethylenepentaamine (HMTEPA).

36. The method of claim 28, wherein the precursor species comprises a precursor for a metal of a ferroelectric material.

37. The method of claim 28, wherein the precursor species comprises a precursor for strontium.

38. The method of claim 28, wherein the precursor species comprises a precursor for bismuth.

39. The method of claim 28, wherein the precursor species comprises a precursor for tantalum.

40. The method of claim 28, wherein the precursor species comprises $Sr(thd)_2$-LBA, where LBA is a Lewis base adducting species.

41. The method of claim 40, wherein the Lewis base adducting species is the same as the Lewis base of the solvent composition.

42. The method of claim 28, wherein the precursor species comprises $Bi(thd)_3$.

43. The method of claim 28, wherein the precursor species comprises $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

44. The method of claim 28, wherein the precursor species comprises $Sr(thd)_2$-LBA, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$, where LBA is a Lewis base adducting species that coordinatively complexes with $Sr(thd)_2$.

45. The method of claim 28, wherein the total solution molarity of the precursor composition is from about 0.3 M to about 0.7 M.

46. A precursor composition useful for liquid delivery MOCVD, comprising SBT precursors dissolved in a solvent system consisting essentially of tetrahydrofuran.

47. The precursor composition of claim 46, wherein the SBT precursors comprise compatible Sr, Bi and Ta beta-diketonates.

48. The precursor composition of claim 47, wherein the SBT precursors comprise a strontium beta-diketonate coordinated to tetrahydrofuran.

49. The precursor composition of claim 48, wherein the SBT precursors comprise a bismuth beta-diketonate.

50. The precursor composition of claim 48, wherein the SBT precursors comprise a tantalum beta-diketonate.

51. The precursor composition of claim 48, wherein the SBT precursors comprise a bismuth beta-diketonate coordinated to tetrahydrofuran.

52. The precursor composition of claim 48, wherein said beta-diketonate includes a β-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; tod; fod; hfod; and corresponding β-thioketonate ligands.

53. The precursor composition of claim 48, wherein the SBT precursors comprise $Sr(thd)_2(THF)_4$.

54. The precursor composition of claim 48, wherein the SBT precursors comprise $Bi(thd)_3$.

55. The precursor composition of claim 48, wherein the SBT precursors comprise $Bi(thd)_3$ coordinated to THF.

56. The precursor composition of claim 48, wherein the SBT precursors comprise $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

57. The precursor composition of claim 48, wherein the SBT precursors comprise $Sr(thd)_2(THF)_4$, $Bi(thd)_3$ and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

58. The precursor composition of claim 48, having a total solution molarity of from about 0.2 M to about 0.6 M.

59. The precursor composition of claim 48, further comprising a dopant precursor.

60. The precursor composition of claim 59, wherein the dopant precursor comprises a niobium beta-diketonate.

61. The precursor composition of claim 60, wherein the niobium beta-diketonate comprises $Nb(O\text{-}i\text{-}Pr)_4(thd)$.

62. The precursor composition of claim 59, wherein the precursors comprise $Sr(thd)_2(THF)_4$, $Bi(thd)_3$, $Ta(O\text{-}i\text{-}Pr)_4(thd)$ and $Nb(O\text{-}i\text{-}Pr)_4(thd)$.

63. The precursor composition of claim 47, wherein said beta-diketonate comprises a β-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; tod; fod; hfod; and corresponding β-thioketonate ligands.

64. The precursor composition of claim 48, wherein said strontium beta-diketonate comprises a β-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; tod; fod; hfod; and corresponding β-thioketonate ligands.

65. The precursor composition of claim 60, wherein said niobium beta-diketonate comprises a β-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; tod; fod; hfod; and corresponding β-thioketonate ligands.

66. The precursor composition of claim 50, wherein said tantalum beta-diketonate comprises a β-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; tod; fod; hfod; and corresponding β-thioketonate ligands.

67. An SBT precursor composition comprising SBT precursors dissolved in tetrahydrofuran, having a boiling point at 1 atmosphere pressure of about 66°C.

68. A precursor composition useful for liquid delivery MOCVD, comprising SBT precursors dissolved in a solvent system comprising tetrahydrofuran and a Lewis base ligand.

69. The precursor composition of claim 68, wherein the Lewis base ligand comprises a ligand selected from the group consisting of ethers, glymes, amines and polyamines.

70. The precursor composition of claim 68, wherein the solvent system comprises from about 90 to about 99 parts by volume THF and from about 1 to about 10 parts by volume Lewis base ligand.

71. The precursor composition of claim 68, wherein the SBT precursors comprise $Sr(thd)_2(pmdeta)$, $Bi(thd)_3(pmdeta)$ and $Ta(O\text{-}i\text{-}Pr)_4(thd)$ and the Lewis base ligand comprises pmdeta.

72. The precursor composition of claim 71, wherein the solvent system comprises about 90 parts by volume THF and about 10 parts by volume pmdeta.

73. A method of forming SBT material on a substrate, comprising:

providing a precursor composition for SBT;

volatilizing the precursor composition to yield a precursor vapor; and

contacting the precursor vapor with the substrate to deposit SBT thereon;

wherein the precursor composition comprises SBT precursors dissolved in a solvent system consisting essentially of tetrahydrofuran.

74. The method of claim 73, wherein the SBT precursors are compatible Sr, Bi and Ta beta-diketonates.

75. The method of claim 74, wherein the SBT precursors comprise a strontium beta-diketonate coordinated to tetrahydrofuran.

76. The method of claim 73, wherein the precursor composition is volatilized by contacting a heated porous vaporization element having an average pore size in the range of from about 50 to about 200 microns.

77. The method of claim 73, wherein the precursor composition is volatilized by contacting a heated porous vaporization element having an average pore size in the range of from about 60 to about 120 micrometers.

78. The method of claim 73, wherein the precursor composition is volatilized by contacting a heated porous vaporization element having an average pore size in the range of from about 80 to about 110 micrometers.

79. The method of claim 73, wherein the precursor vapor is mixed with a helium carrier gas to form a carrier gas mixture for said contacting with the substrate to deposit SBT thereon.

80. A method of forming an SBT film on a substrate, comprising liquid delivery MOCVD using a precursor composition comprising SBT precursors dissolved in a solvent system consisting essentially of tetrahydrofuran.

81. The precursor composition of claim 80, wherein the SBT precursors comprise compatible Sr, Bi and Ta beta-diketonates.

82. The precursor composition of claim 81, wherein the SBT precursors comprise a strontium beta-diketonate coordinated to tetrahydrofuran.

83. The method of claim 81, wherein the SBT precursors include $Sr(thd)_2(THF)_4$, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

84. The method of claim 81, having a total solution molarity of the precursor composition of from about 0.2 M to about 0.6 M.

85. The method of claim 81, wherein the precursor composition has a boiling point in the range of from about 60 to about 75°C.

86. The method of claim 81, wherein the precursor composition comprises $Sr(thd)_2(THF)_4$.

87. The method of claim 81, wherein the precursor composition comprises $Bi(thd)_3$.

88. The method of claim 81, wherein the precursor composition comprises $Ta(O\text{-}i\text{-}Pr)_4(thd)$.

89. The method of claim 81, wherein the beta-diketonate ligand comprises a ligand selected from the group consisting of: acac; hfac; tfac; thd; fod; tod; hfod; and corresponding β-thioketonate ligands.

90. The method of claim 80, wherein the precursor composition comprises a bismuth beta-diketonate.

91. The method of claim 90, wherein said bismuth beta-diketonate includes a beta-diketonate ligand selected from the group consisting of: acac; hfac; tfac; thd; fod; tod; hfod; and corresponding β-thioketonate ligands.

92. The method of claim 81, wherein the SBT precursors comprise a bismuth beta-diketonate coordinated to tetrahydrofuran.

93. The method of claim 81, wherein the precursor composition has a boiling point at 1 atmosphere pressure of about 66°C.

94. The method of claim 81, wherein the precursor composition is volatilized to form a precursor vapor, by contacting a heated porous vaporization element having an average pore size in the range of from about 50 to about 200 microns.

95. The method of claim 81, wherein the precursor composition is volatilized to form a precursor vapor, by contacting a heated porous vaporization element having an average pore size in the range of from about 60 to about 120 micrometers.

96. The method of claim 81, wherein the precursor composition is volatilized to form a precursor vapor, by contacting a heated porous vaporization element having an average pore size in the range of from about 80 to about 110 micrometers.

97. The method of claim 95, wherein the precursor vapor is mixed with a helium carrier gas to form a carrier gas mixture for contacting a substrate to deposit SBT thereon.

98. The method of claim 96, wherein the precursor vapor is mixed with a helium carrier gas to form a carrier gas mixture for contacting a substrate to deposit SBT thereon.

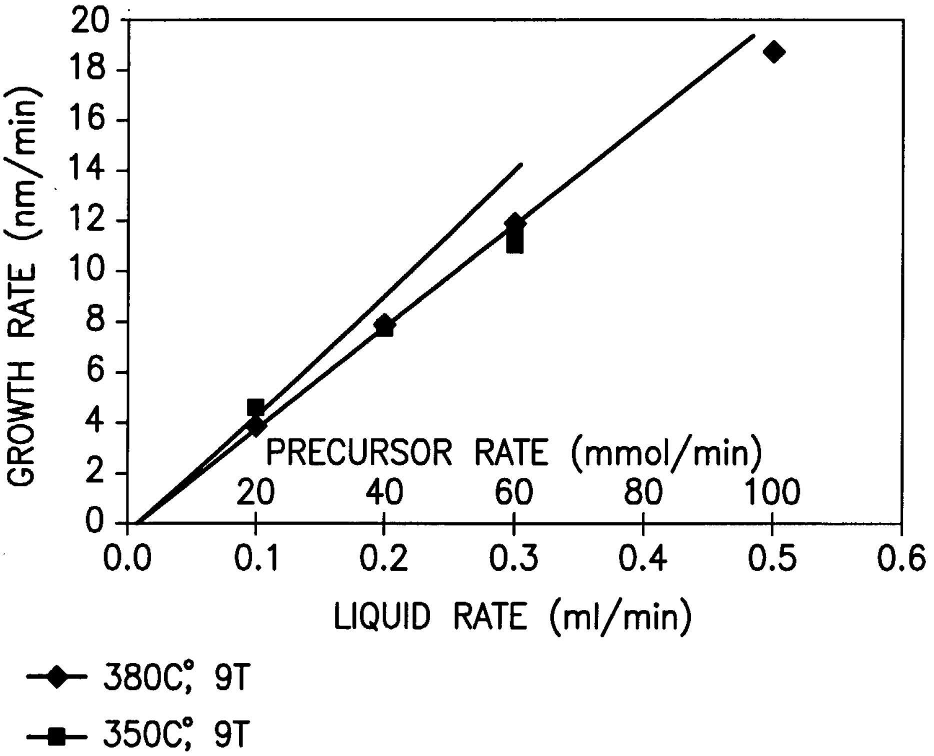

GROWTH RATE (nm/min)
20
18
16
14
12
10
8
6
4
2
0
PRECURSOR RATE (mmol/min)
20
40
60
80
100
0.0
0.1
0.2
0.3
0.4
0.5
0.6
LIQUID RATE (ml/min)
◆ 380C°, 9T
■ 350C°, 9T

FIG.1

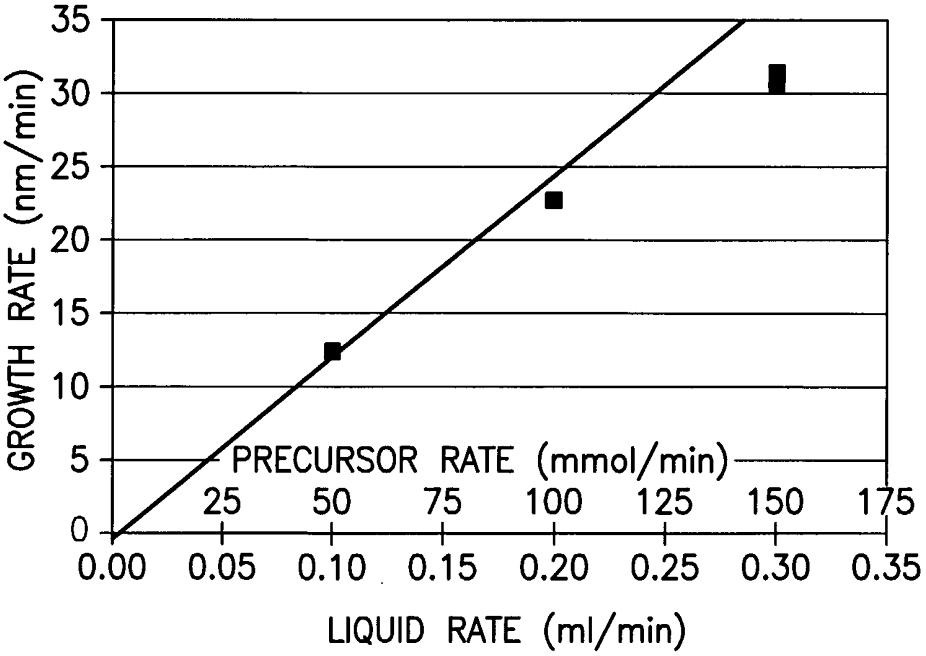

GROWTH RATE (nm/min)
35
30
25
20
15
10
5
0
PRECURSOR RATE (mmol/min)
25
50
75
100
125
150
175
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
LIQUID RATE (ml/min)

FIG.2

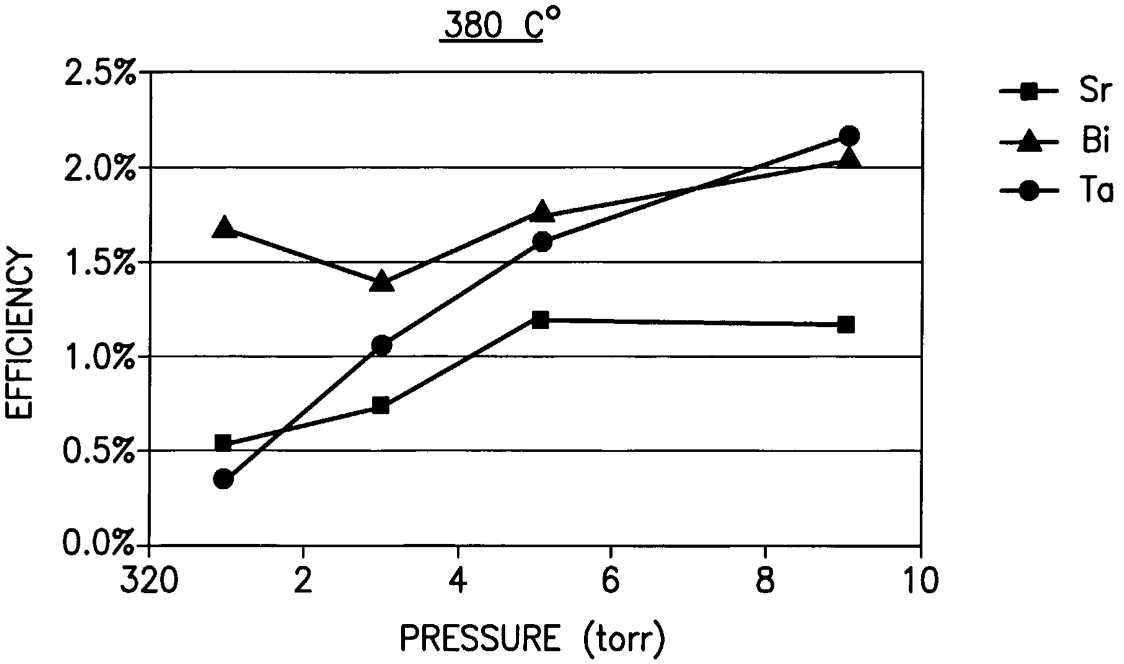

380 C°
2.5%
2.0%
1.5%
1.0%
0.5%
0.0%
EFFICIENCY
320
2
4
6
8
10
PRESSURE (torr)
Sr
Bi
Ta

FIG.3

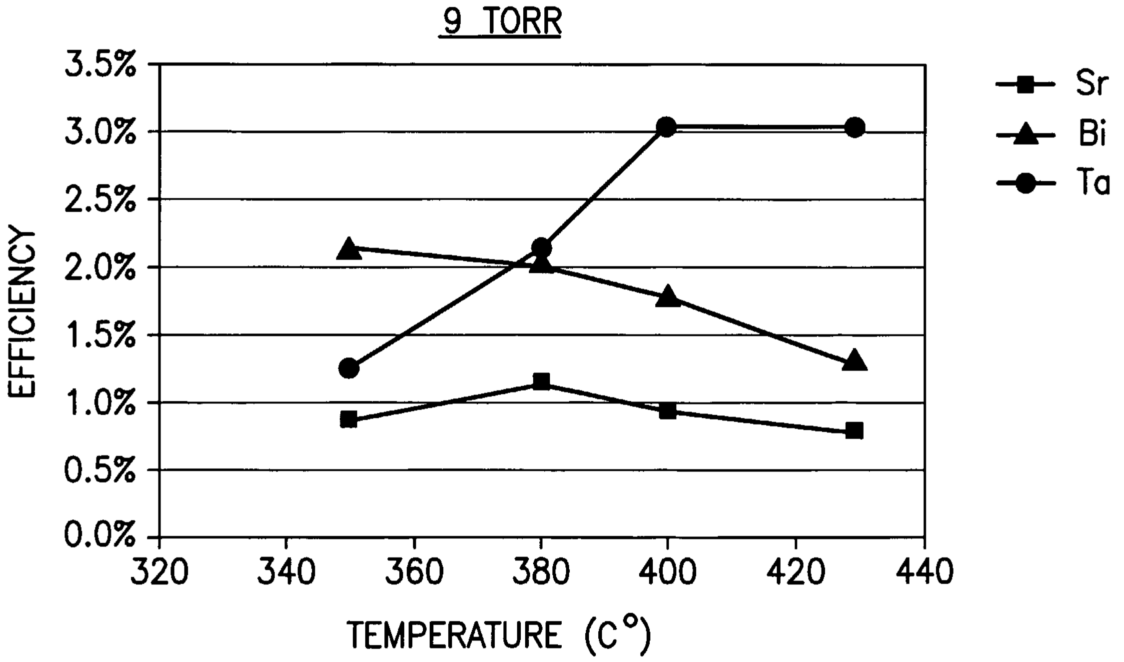

9 TORR
3.5%
3.0%
2.5%
2.0%
1.5%
1.0%
0.5%
0.0%
EFFICIENCY
320
340
360
380
400
420
440
TEMPERATURE (C°)
Sr
Bi
Ta

FIG.4

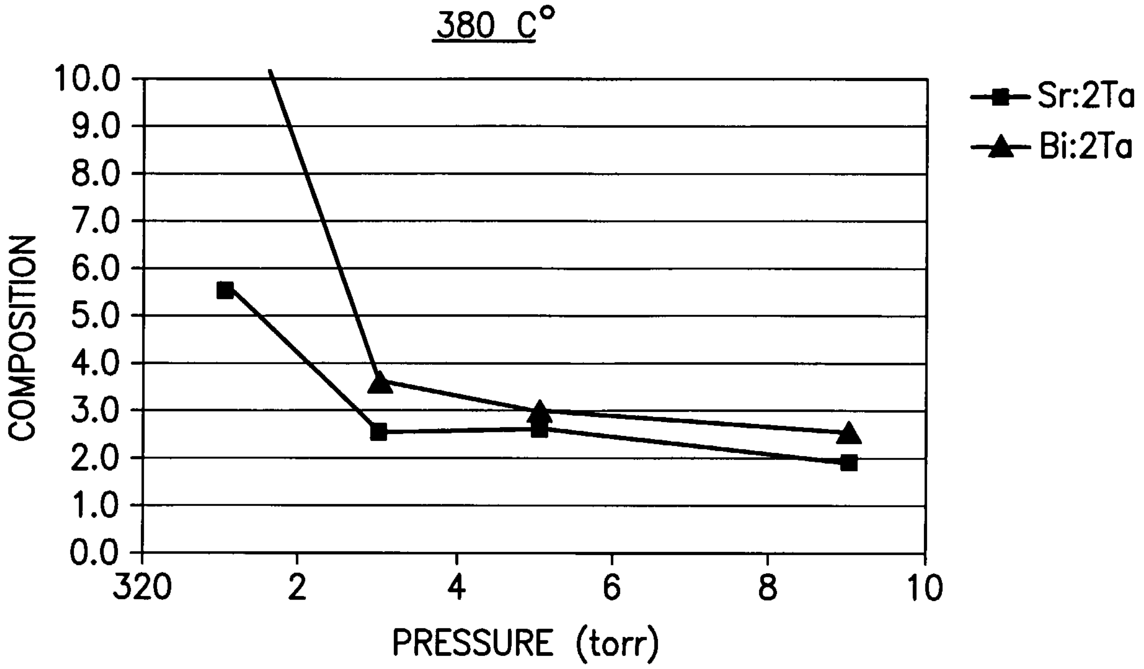

380 C°
COMPOSITION
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
320
2
4
6
8
10
PRESSURE (torr)
Sr:2Ta
Bi:2Ta

FIG.5

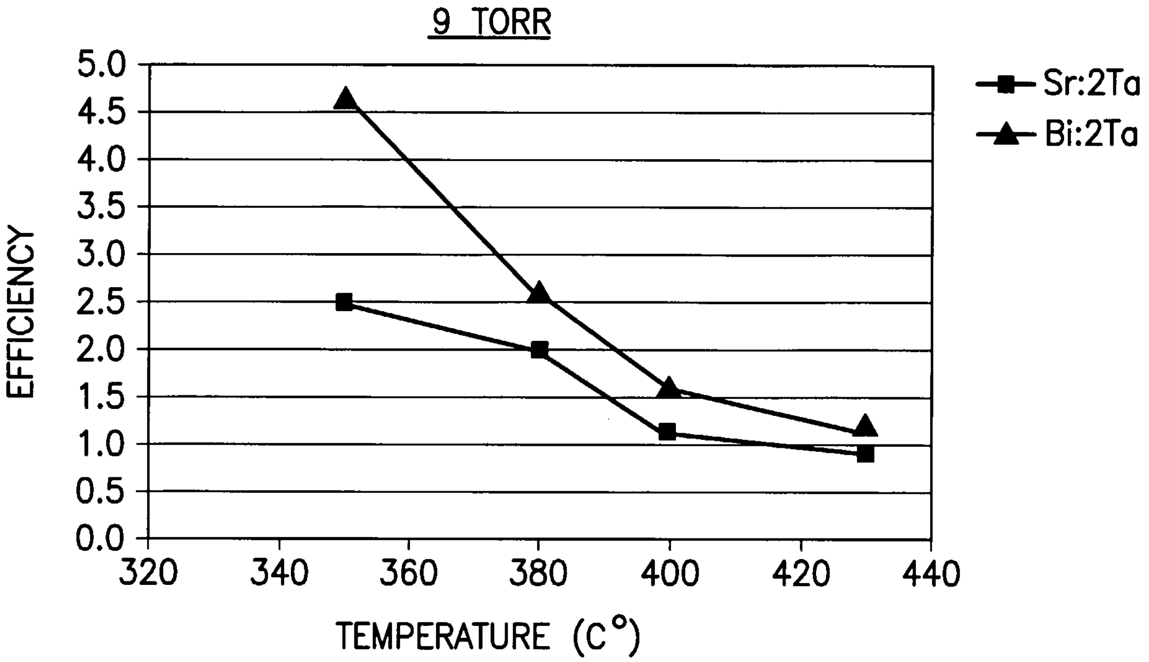

9 TORR
EFFICIENCY
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
320
340
360
380
400
420
440
TEMPERATURE (C°)
Sr:2Ta
Bi:2Ta

FIG.6

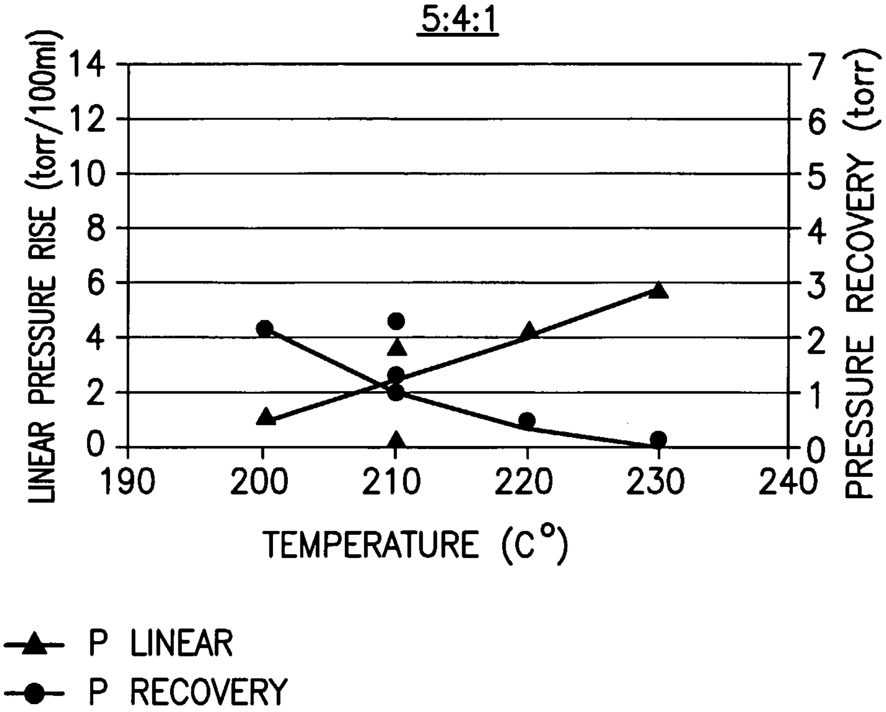

5:4:1
LINEAR PRESSURE RISE (torr/100ml)
14
12
10
8
6
4
2
0
PRESSURE RECOVERY (torr)
7
6
5
4
3
2
1
0
190
200
210
220
230
240
TEMPERATURE (C°)
P LINEAR
P RECOVERY

FIG.7

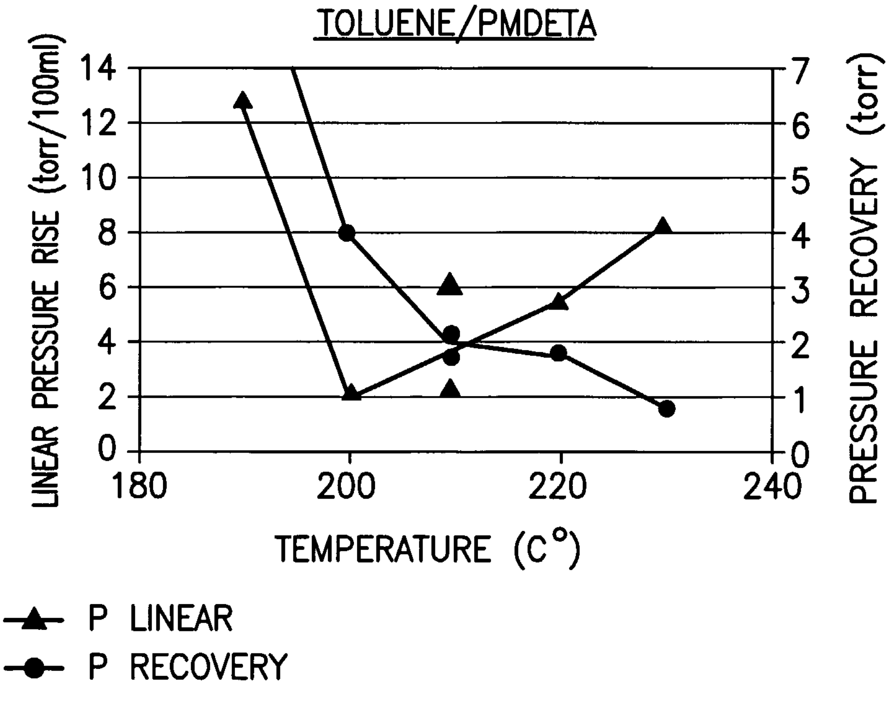

TOLUENE/PMDETA
LINEAR PRESSURE RISE (torr/100ml)
14
12
10
8
6
4
2
0
PRESSURE RECOVERY (torr)
7
6
5
4
3
2
1
0
180
200
220
240
TEMPERATURE (C°)
P LINEAR
P RECOVERY

FIG.8

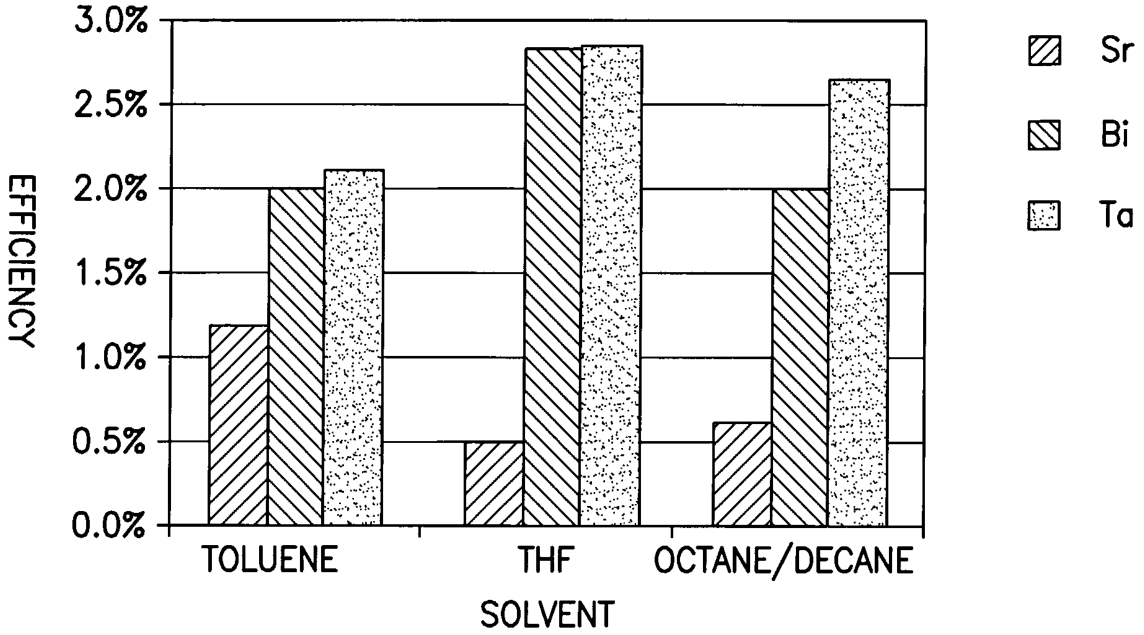

3.0%
2.5%
2.0%
1.5%
1.0%
0.5%
0.0%
EFFICIENCY
TOLUENE
THF
OCTANE/DECANE
SOLVENT
Sr
Bi
Ta

FIG.9

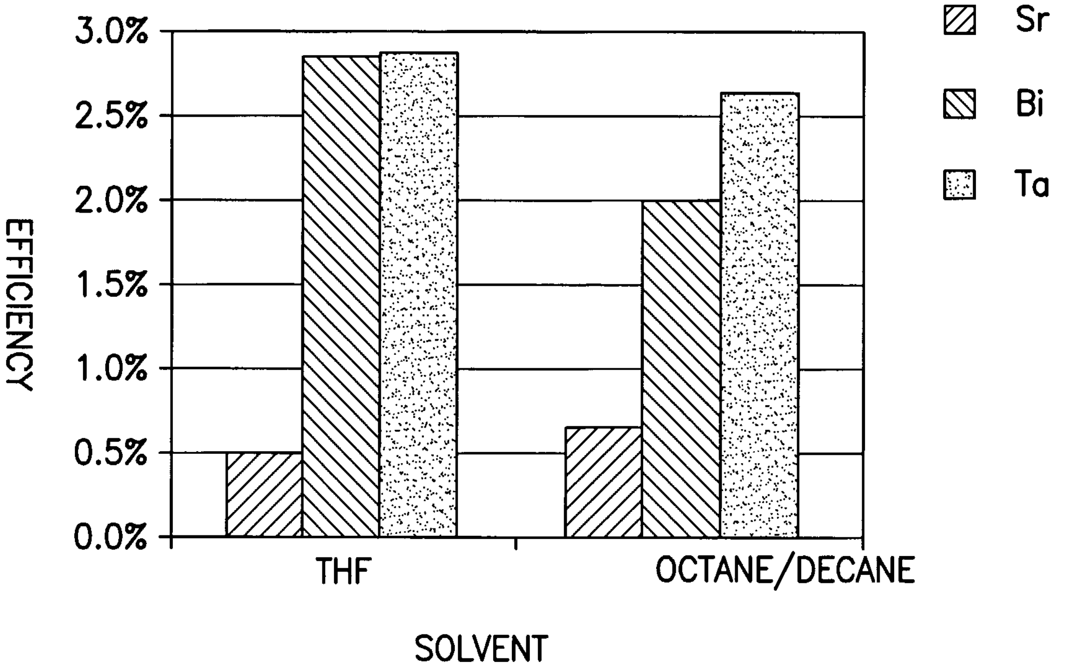

3.0%
2.5%
2.0%
1.5%
1.0%
0.5%
0.0%
EFFICIENCY
THF
OCTANE/DECANE
SOLVENT
Sr
Bi
Ta

FIG.10

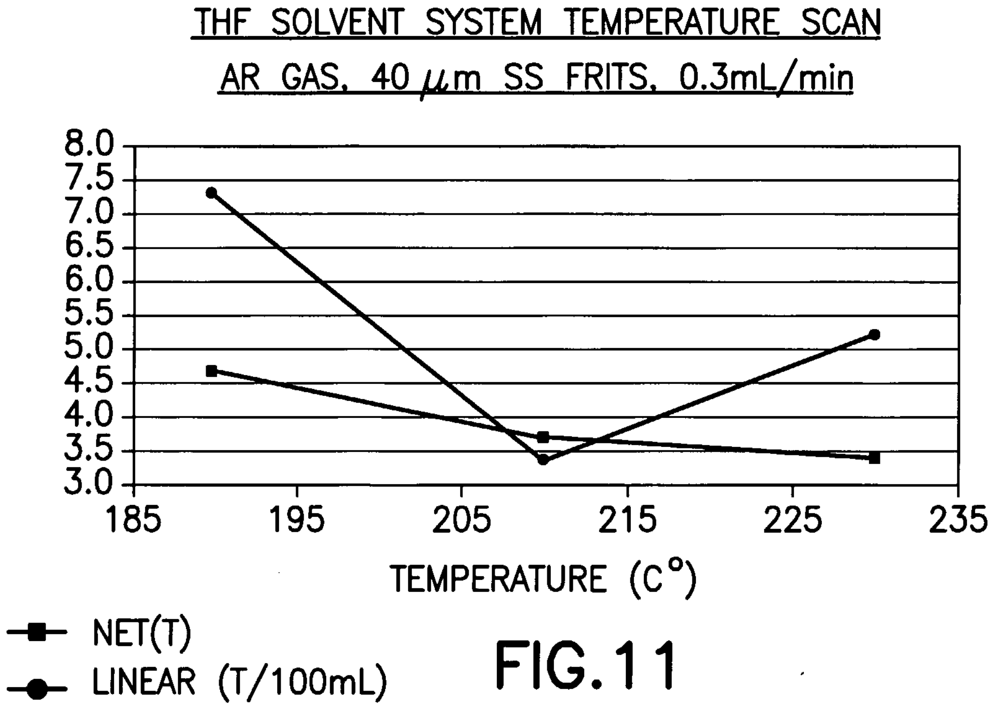

THF SOLVENT SYSTEM TEMPERATURE SCAN
AR GAS, 40 μm SS FRITS, 0.3mL/min
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
185
195
205
215
225
235
TEMPERATURE (C°)
NET(T)
LINEAR (T/100mL)

FIG.11

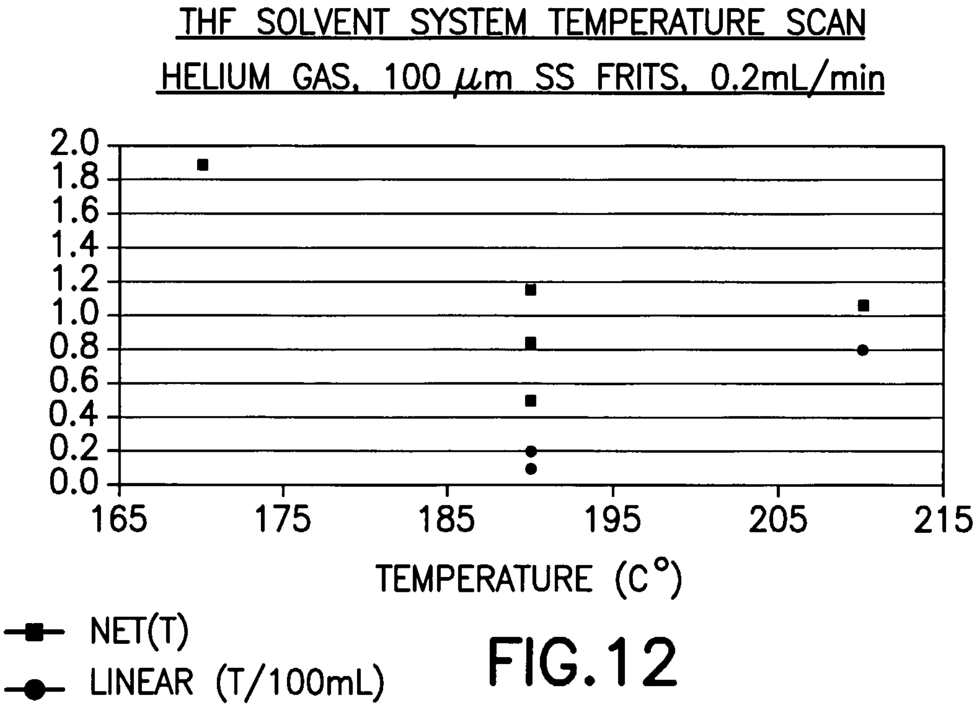

THF SOLVENT SYSTEM TEMPERATURE SCAN
HELIUM GAS, 100 μm SS FRITS, 0.2mL/min
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
165
175
185
195
205
215
TEMPERATURE (C°)
NET(T)
LINEAR (T/100mL)

FIG.12

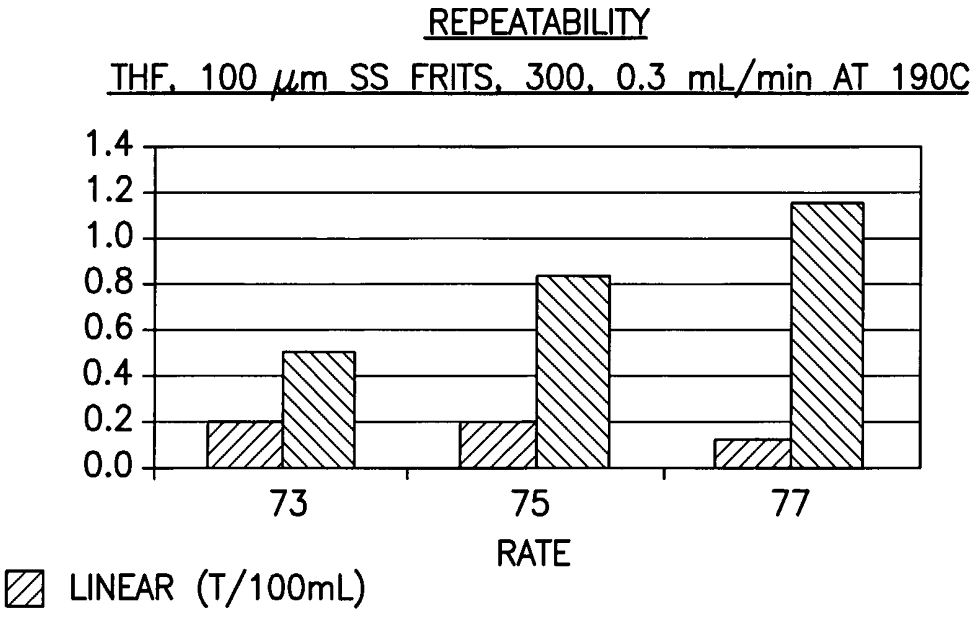

REPEATABILITY
THF, 100 μm SS FRITS, 300, 0.3 mL/min AT 190C
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
73
75
77
RATE
▨ LINEAR (T/100mL)
▧ NET(T)

FIG.13

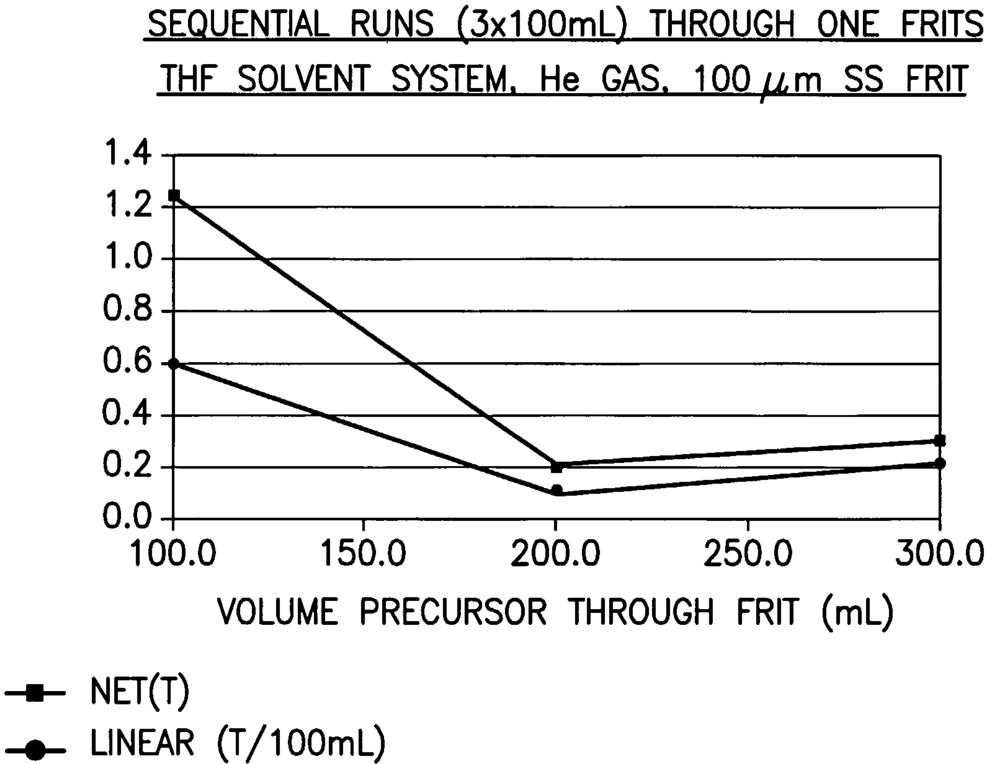

SEQUENTIAL RUNS (3x100mL) THROUGH ONE FRITS
THF SOLVENT SYSTEM, He GAS, 100 μm SS FRIT
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100.0
150.0
200.0
250.0
300.0
VOLUME PRECURSOR THROUGH FRIT (mL)
NET(T)
LINEAR (T/100mL)

FIG.14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/29299

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C23C 16/40; C09K 3/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/364; 106/287.18, 287.2, 287.21, 287.3, 287.23, 311; 427/255.32, 901

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - Y	Ami et al., Materials Research Society Symposium Proceedings, Vol. 415, 1996, pp. 195-200, especially page 195.	1, 46, 67, 73, 80 ---- 47-66, 74-79, 81-98
Y	US 5,453,494 A (KIRLIN et al.) 26 September 1995, col. 8, lines 56-66.	22, 23, 40, 41, 48-62, 64-66, 71, 72, 75, 82, 83, 86, 92
X - Y	US 5,478,610 A (DESU et al.) 26 December 1995, col. 8, line 57 to col. 9, line 25.	68-70 -- 47-66, 71, 72, 74, 75, 81-98

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search

15 JANUARY 2001

Date of mailing of the international search report

31 JAN 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
TIMOTHY MEEKS
Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/29299

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - Y	US 5,629,229 A (SI et al) 13 May 1997, col. 6, line 60 to col. 7, line 35.	1-19, 28-37 -- 22, 23, 40, 41
Y	US 5,677,002 A (KIRLIN et al.) 14 October 1997, col. 6, lines 19-45.	50, 56, 57, 60-62, 65, 66
Y	US 5,900,279 A (HIDEAKI et al.) 4 May 1999, Col. 3, lines 25-35 and col. 3, line 64 to col. 4, line 20	22, 23
P,X - P,Y	US 6,111,124 A (BAUM et al.) 29 August 2000, col. 2, lines 30-40 and cols. 6 and 7.	1-45, 68-70 -- 71, 72

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/29299

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

252/364; 106/287.18, 287.2, 287.21, 287.3, 287.23, 311; 427/255.32, 901