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(54) Title: METHOD OF FORMING FUNCTIONALIZED SILANES

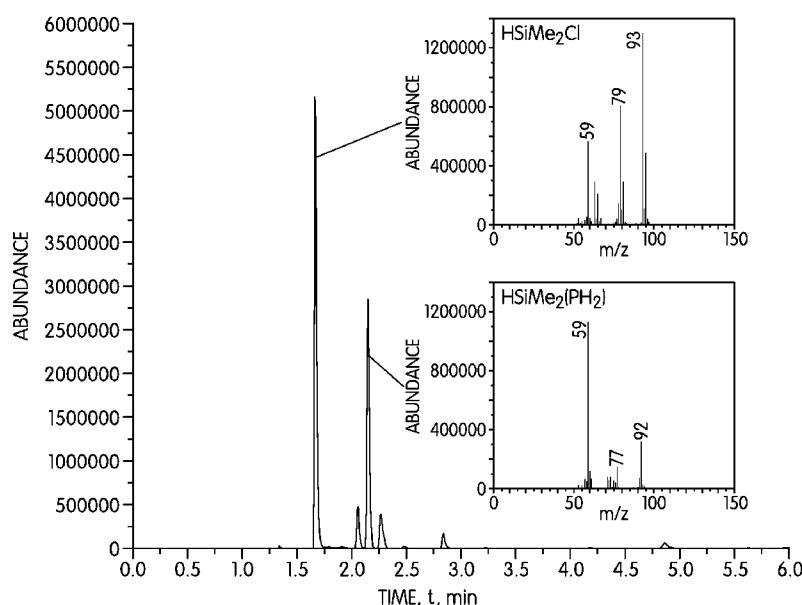


FIG. 3

(57) Abstract: Heteroatom doped silane compounds, e.g., phosphorus-containing silane compounds, are provided. The application also provides methods of producing the heteroatom doped silane compounds from halogen substituted silanes via reaction with a heteroatom-containing nucleophile.



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METHOD OF FORMING FUNCTIONALIZED SILANES

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] The present application claims the benefit of priority of U.S. Provisional Patent Application No. 61/130,271, entitled Method of Forming Functionalized Silanes, filed on May 29, 2008, the disclosure of which is incorporated by reference herein in its entirety.

GOVERNMENT RIGHTS STATEMENT

[0002] This work was supported in part by the Defense Microelectronics Activity under grant DMEA H94003-08-2-0801 and the National Science Foundation under grant EPS-0447679. The U.S. Government has a paid-up license in this invention and the right in certain limited circumstances to require the patent owner to license others on reasonable terms, including as provided for by the terms of the grant awarded by the Department of Defense.

BACKGROUND

[0003] While polymers have been a focus of evaluation as flexible layers in electronic materials, more recently there has been an interest in developing printed routes to inorganic semiconductors as a means of achieving higher mobilities. To utilize cost-effective polymeric substrates in a roll-to-roll manufacturing environment, low-temperature atmospheric pressure deposition routes to semi-conductors with desirable electrical properties are required. Cyclic silanes, such as cyclohexasilane, have been shown to be useful in liquid silane precursors to a-Si:H rectifying diodes and field effect transistors. The liquid cyclic silanes reportedly can be transformed into amorphous silicon and subsequently to crystalline Si under appropriate conditions. The initial studies reported potential non-uniform dopant distribution, when simple inorganic boron or phosphorus compounds, which may tend to congregate at the film surface, when employed as dopants. Such non-uniform doping may lead to suboptimal electrical properties in the resulting semi-conductor film. The availability of liquid silanes which contain one or more heteroatom dopants covalently bound to a silane backbone offer the potential to provide good miscibility with other silanes and permit atomic level mixing and uniform dopant distributions.

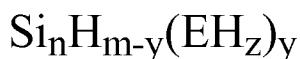
SUMMARY

[0004] The present application is directed to heteroatom doped silane compounds and methods of producing such compounds. The methods commonly includes reacting a

halogen substituted silane with a nucleophilic reagent to form a doped silane with a Si-E bond, where “E” may be selected from Group 13, Group 14, Group 15 and/or Group 16 elements. The doped silane is desirably a liquid under ambient temperature and pressure conditions (e.g., under 1 atmosphere pressure at 298 °C).

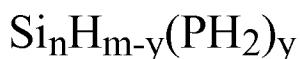
[0005] The halogen substituted silane may be formed by reacting a cyclic or acyclic silane with a halogenating reagent. In other embodiments, the halogen substituted silane may be formed by reacting an aryl substituted (e.g., phenyl substituted) cyclic or acyclic silane with a hydrogen halide in the presence of a Lewis acid catalyst, such as AlCl₃. In certain embodiments, it may be advantageous to control the starting materials, reaction conditions and/or stoichiometry, such that the reaction product is predominantly a monohalogen substituted and/or dihalogen substituted silane. Monohalogen substituted cyclic silanes, such as monochlorocyclopentasilane, monochlorocyclohexasilane, monobromocyclopentasilane and monobromocyclohexasilane, may be particularly desirable as intermediates for use in producing the present doped silane compounds.

[0006] The present heteroatom doped silane compounds may have the formula:



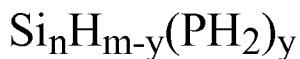
wherein n is an integer greater than 2; m is an integer from 2n – 2 to 2n + 2; y is an integer from 1 to n; z is 2 or 3; and E is selected from Group 13, Group 14, Group 15 and/or Group 16 elements.

[0007] Examples of the present heteroatom doped silane compounds include cyclic silane compounds having the formula:



wherein n is an integer greater than 2 (commonly 3 to 10); m is 2n – 2 or 2n; and y is an integer from 1 to n.

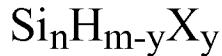
[0008] Other examples of the present heteroatom doped silane compounds include acyclic silane compounds (e.g., branched and/or linear silanes), which are desirably a liquid under ambient temperature and pressure, having the formula:



wherein n is an integer greater than 2; m is 2n + 2; and y is an integer from 1 to n.

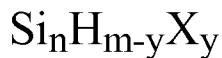
[0009] In certain embodiments, it may be advantageous to produce doped silane compounds which only have one or two heteroatoms per molecule. Suitable synthetic

intermediates which may be used to produce such heteroatom doped silane compounds include halogen substituted cyclic silane compounds having the formula:



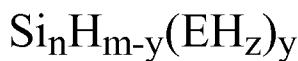
wherein n is an integer greater than 2 (commonly about 3 to 10); m is an integer from $2n - 2$ to $2n$; y is 1 or 2; and each X independently represents a halogen atom. Suitable examples include mono- or dihalogenated derivatives of cyclotrisilane, cyclopentasilane, cyclohexasilane, silylcyclopentasilane, silylcyclohexasilane and spiro[4.4]nonasilane.

[0010] In certain embodiments, the present heteroatom doped silane compounds may be prepared by reacting a mixture comprising:



with a nucleophile of the formula: $\text{M}(\text{EH}_z)_a$

to provide a doped silane compound of the formula:

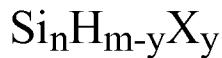


In the above formulas, n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; y is an integer from 1 to n. E is a heteroatom chosen from Group 13, Group 14, Group 15 and/or Group 16 elements; z is 2 or 3; a is an integer from 1 to 4; and M is a metal atom containing moiety. The reaction is typically carried out in the presence of a solvent, e.g., an ether solvent such as glyme, diglyme or the like. For example, the halogenated silane may be reacted with a nucleophile of the formula:

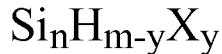


Suitable examples of such nucleophiles include NaPH_2 , LiPH_2 , $\text{NaAl}(\text{PH}_2)_4$ and $\text{LiAl}(\text{PH}_2)_4$.

[0011] In certain embodiments, the present application provides a method of producing a halogenated cyclic silane of the formula:

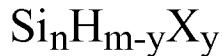


wherein n is an integer greater than 2 (commonly about 3 to 10); m is $2n - 2$ or $2n$; y is 1 or 2; and each X independently represents a halogen atom. The method includes reacting a cyclic silane (e.g., either a monocyclic or bicyclic) with a halogenating agent to provide a halo-silane having a formula:



wherein n is an integer greater than 2 (commonly about 3 to 10; m is an integer from $2n - 2$ to $2n$; y is 1 or 2; and each X independently represents a halogen atom. Examples of suitable halogenating agents include AgCl, HgCl₂, HgBr₂, N-chlorosuccinimide (“NCS”), N-bromosuccinimide (“NBS”), SnCl₄ and iodine (I₂).

[0012] In other embodiments, heteroatom doped silane compounds may be prepared by reacting a mixture comprising:



with other phosphorus-containing nucleophiles. For example, halogenated silanes may be reacted with phosphorus-containing nucleophiles of the formula:

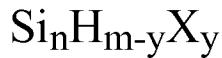


where M* is an alkali metal (e.g., Li) to provide a heteroatom doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n (and often desirably 1 or 2).

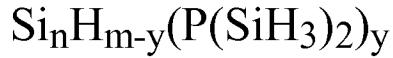
[0013] In certain other embodiments, heteroatom doped silane compounds may be prepared by reacting a mixture comprising:



with phosphorus-containing nucleophiles of the formula:



where M* is an alkali metal (e.g., Li) to provide a heteroatom doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n (and often desirably 1 or 2).

BRIEF DESCRIPTION OF THE FIGURES

[0014] Figure 1 depicts a GC-MS of the product solution produced according to the procedure described in Example 1.

[0015] Figure 2 depicts GC-MS of the product solution produced according to the procedure described in Example 2.

[0016] Figure 3 depicts GC-MS of the product solution produced according to the procedure described in Example 2 displaying Si-P bond formation.

DETAILED DESCRIPTION

[0017] The present heteroatom doped silane compounds may be produced by reacting a halogen substituted silane with a nucleophilic reagent to form the doped silane. For example, a halogenated silane may be reacted with a phosphorus-containing nucleophile to form a compound which includes a Si-P bond. The resulting product, a phosphorus doped silane, is desirably a liquid under ambient temperature and pressure (e.g., under 1 atmosphere pressure at 298°C).

[0018] The halogen substituted silane may be formed by reacting a cyclic or acyclic silane with a halogenating reagent. In some embodiments, the starting materials, reaction conditions and/or stoichiometry may be controlled such that the reaction product is predominantly a silane substituted with only one or two halogen atoms. The halogenation reaction is typically carried out in the presence of a solvent, e.g., a chlorinated hydrocarbon solvent such as methylene chloride, chloroform, carbon tetrachloride and/or dichloroethane.

[0019] In some embodiments, the halogen substituted silane may be formed by dissolving a silane compound, e.g., a cyclic silane such as cyclotrisilane, cyclopentasilane or cyclohexasilane, in a chlorinated solvent (e.g., methylene chloride) and stirring the solution of silane with an inorganic halogenating reagent, such as AgCl, HgCl₂, HgBr₂, BCl₃, or SnCl₄. In such cases, an excess of the halogenating reagent may be used. After stirring the reaction mixture for a period of several hours, a mixture containing mono- and dihalogenated silane is typically obtained.

[0020] In other embodiments, a silane compound, e.g., a cyclic silane such as cyclotrisilane, cyclopentasilane or cyclohexasilane, may be dissolved in a chlorinated solvent (e.g., methylene chloride or carbon tetrachloride) and a stoichiometric amount of N-chlorosuccinimide (“NCS”) or N-bromosuccinimide (“NBS”) added to the solution. By stoichiometric amount is meant that one equivalent of the halogenating reagent is added for

each halogen desired to be added to the silane. For example, if monohalogenated silanes are the desired products, one mole of NBS or NCS is added to the solution for each mole of silane. If dihalogenated silanes are the desired products, two moles of NBS or NCS are added to the solution for each mole of silane.

[0021] Examples of suitable halogenated silane intermediates include:

cyclotrisilane having 1 or 2 halogen atoms attached thereto;
cyclopentasilane having 1 or 2 halogen atoms attached thereto;
cyclohexasilane having 1 or 2 halogen atoms attached thereto;
silylcyclopentasilane having 1 or 2 halogen atoms attached thereto;
silylcyclohexasilane having 1 or 2 halogen atoms attached thereto; and
spiro[4.4]nonasilane having 1 or 2 halogen atoms attached thereto.

[0022] Halogenated silane compounds, which may be used to produce the present heteroatom doped silane compounds may be produced by reacting a halogenating reagent with a corresponding silane precursor. Examples of suitable halogenating reagents include:

AgCl, HgCl₂, HgBr₂, SnCl₄, I₂, N-chlorosuccinimide (“NCS”), and
N-bromosuccinimide (“NBS”).

[0023] Examples of suitable phosphorus-containing nucleophiles which may be used to produce the present heteroatom doped silane compounds include:

LiPH₂, NaPH₂, KPH₂, LiAl(PH₂)₄, NaAl(PH₂)₄,
LiHPSiH₃, LiP(SiH₃)₂ and LiAl(PHSiH₃)₄.

Examples

[0024] Reference is made in the following to a number of illustrative examples of methods of producing the present compositions. The following embodiments should be considered as only an illustration of such methods and compositions and should not be considered to be limiting in any way.

Example 1: AgCl route towards Si₆H_{12-n}Cl_n (where n = 1, 2)

[0025] The desired chlorosilane product, Si₆H_{12-n}Cl_n (where n = 1, 2) was prepared by dissolving 185.5 mg (1.03 mmol, 1.00 eq) of cyclohexasilane, Si₆H₁₂, in 2 mL of methylene chloride (CH₂Cl₂) to which an excess amount (515.4 mg, 3.60 mmol, 3.50 eq) of silver chloride, AgCl, was added as a solid with vigorous stirring. The reaction mixture was allowed to stir in the dark as a consequence of the light sensitivity of silver compounds. After stirring for 3.5 h at room temperature (25°C) the reaction mixture was a dark grey

color which was indicative of silver metal, Ag^0 , forming. This mixture was filtered to remove the grey colored precipitate (ppt) yielding a clear colorless solution. This product solution was analyzed by GC-MS (see Figure 1) which established that 69.1% of the Si_6H_{12} was converted to the mono-chlorocyclohexasilane, $\text{Si}_6\text{H}_{11}\text{Cl}$, and 11.8% was converted to the dichlorocyclohexasilane, $\text{Si}_6\text{H}_{10}\text{Cl}_2$. Therefore, 19.1% of the Si_6H_{12} starting material remained unreacted.

Example 2: HgCl_2 route towards $\text{Si}_6\text{H}_{12-n}\text{Cl}_n$ (where $n = 1, 2$)

[0026] The desired chlorosilane product, $\text{Si}_6\text{H}_{12-n}\text{Cl}_n$ (where $n = 1, 2$) was prepared by dissolving 217.5 mg (1.20 mmol, 1.00 eq) of Si_6H_{12} in 5 mL of CH_2Cl_2 to which an excess amount (1.31 g, 4.81 mmol, 4.00 eq) of mercury(II) chloride, HgCl_2 , was slowly added as a solid with vigorous stirring. Initially there appeared to be no observable reaction, therefore, the reaction mixture was allowed to stir. Overnight liquid mercury had formed suggesting the desired reaction had taken place. The solution mixture was filtered to remove unreacted HgCl_2 . This was done by careful decantation of the solution mixture from the liquid mercury byproduct that formed. Once filtered the filtrate was a clear colorless solution. The product solution was analyzed by GC-MS (Figure 2) concluding that 91.5% of the Si_6H_{12} was converted into $\text{Si}_6\text{H}_{11}\text{Cl}$ and 7.6% converted to $\text{Si}_6\text{H}_{10}\text{Cl}_2$. Therefore, 0.9% of unreacted Si_6H_{12} was remaining.

Example 3: SnCl_4 route towards $\text{Si}_6\text{H}_{12-n}\text{Cl}_n$ (where $n = 1, 2$)

[0027] The desired chlorosilane product, $\text{Si}_6\text{H}_{12-n}\text{Cl}_n$ (where $n = 1, 2$) was prepared by first dissolving 2.40 g (13.33 mmol) of Si_6H_{12} in 30 mL of CH_2Cl_2 in a 100 mL flask. This solution was then cooled to -10°C at which point an excess of SnCl_4 (5.20 g, 20 mmol) was added into the mixture. The reaction was stirred vigorously for two minutes and then stored in freezer (-10°C) for two days. White precipitate formed was removed by filtration and the filtrate was distilled under vacuum to give 1.8 g colorless liquid. The product liquid was analyzed by GC-MS concluding that 65% of the Si_6H_{12} was converted into $\text{Si}_6\text{H}_{11}\text{Cl}$ and 5% converted to $\text{Si}_6\text{H}_{10}\text{Cl}_2$. Therefore, 30% of unreacted Si_6H_{12} was remaining.

Example 4: Formation of $\text{H}_2\text{PHSiMe}_2$ via $\text{NaAl}(\text{PH}_2)_4$

[0028] $\text{NaAl}(\text{PH}_2)_4$ was synthesized by reacting 50.4 mg of NaPH_2 (0.90 mmol, 1.00 eq) suspended in 2 mL of diethylene glycol dimethyl ether (diglyme) with 30.8 mg of AlCl_3 (0.231 mmol, 3.90 eq) dissolved in 1 mL which resulted in the formation of a cloudy white slurry. This white precipitate is consistent with the formation of sodium chloride, NaCl . The AlCl_3 was quantitatively transferred by washing the vial with 3 x 1 mL of diglyme resulting in a 6 mL mixture that was allowed to stir overnight. After stirring overnight the

reaction mixture was filtered yielding a faint yellow clear filtrate and a white solid. The solids were washed with 3 x 1 mL diglyme to quantitatively transfer the desired product in solution. To this stirring solution of NaAl(PH₂)₄, 103 μ L of chlorodimethylsilane (0.852 g/mL, 0.93 mmol, 4.01 eq), HSiMe₂Cl, was added via micro-syringe addition resulting in the formation of a cloudy solution. The cloudiness is due to the formation of the NaCl byproduct. The mixture was allowed to stir for 10 min after which was filtered yielding a faint yellow product solution. This product filtrate was analyzed by GC-MS (Figure 3) and showed the formation of the desired Si-P containing product of H₂PHSiMe₂.

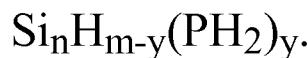
Illustrative Embodiments:

[0029] Reference is made in the following to a number of illustrative embodiments of the subject matter described herein. The following embodiments describe illustrative embodiments that may include various features, characteristics, and advantages of the subject matter as presently described. Accordingly, the following embodiments should not be considered as being comprehensive of all of the possible embodiments or otherwise limit the scope of the methods materials and coatings described herein.

[0030] One embodiment provides a method of preparing a doped silane which includes reacting a mixture comprising:



to provide a heteroatom doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from 2n - 2 to 2n + 2; y is an integer from 1 to n; each X is independently a halogen atom; and M is a metal atom containing moiety. Suitable examples of MPH₂ include:



[0031] In this embodiment, the method may include reacting $\text{Si}_n\text{H}_{2n-y}\text{X}_y$ with NaPH_2

or reacting $\text{Si}_n\text{H}_{2n-y}\text{X}_y$ with $\text{NaAl}(\text{PH}_2)_4$; e.g., reacting



$\text{Si}_7\text{H}_{13}\text{Cl}$ with $\text{NaAl}(\text{PH}_2)_4$.

[0032] In another embodiment, a heteroatom doped silane compound may be formed by reacting a mixture, which includes:

$\text{Si}_n\text{H}_{m-y}\text{X}_y$ and $\text{LiP}(\text{SiH}_3)_2$

to provide a heteroatom doped silane having a formula:

$\text{Si}_n\text{H}_{m-y}(\text{P}(\text{SiH}_3)_2)_y$

wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n.

[0033] In another embodiment, a heteroatom doped silane compound may be formed by reacting a mixture, which includes:

$\text{Si}_n\text{H}_{m-y}\text{X}_y$ and LiPHSiH_3

to provide a heteroatom doped silane having a formula:

$\text{Si}_n\text{H}_{m-y}(\text{PHSiH}_3)_y$

wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n.

[0034] Suitable examples of the present heteroatom doped silane compounds include doped silanes having a formula:

$\text{Si}_n\text{H}_{m-y}(\text{PH}_2)_y$

wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n, often y is 1 or 2. The present heteroatom doped silane compounds may desirably include compounds having one or more of the following formulas:

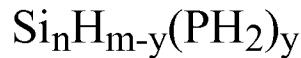
$\text{Si}_6\text{H}_{11}(\text{PH}_2)$;

$\text{Si}_6\text{H}_{10}(\text{PH}_2)_2$;

$\text{Si}_5\text{H}_9(\text{PH}_2)$; and

$\text{Si}_5\text{H}_8(\text{PH}_2)_2$.

[0035] Other examples of the present heteroatom doped silane compounds include doped cyclic silanes having a formula:



wherein n is an integer from 3 to 10; m is $2n - 2$ or $2n$; and y is an integer from 1 to n.

[0036] Other examples of the present heteroatom doped silane compounds include doped silanes having a formula:



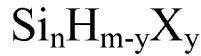
wherein n is an integer greater than 2 (typically 3 to 10); m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n (and often desirably 1 or 2).

[0037] Other examples of the present heteroatom doped silane compounds include doped silanes having a formula:



wherein n is an integer greater than 2 (typically 3 to 10); m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n (and often desirably 1 or 2).

[0038] Certain embodiments provide halogen substituted cyclic silanes having the formula:



wherein n is an integer greater than 2 (commonly 3 to 10); m is $2n$ or $2n - 2$; y is 1 or 2; and each X independently represents a halogen atom. Suitable examples include:

such halogen substituted cyclic silanes wherein n is 3; m is 6; y is 1; and X is a chlorine atom;

such halogen substituted cyclic silanes wherein n is 5; m is 10; y is 1; and X is a chlorine atom;

such halogen substituted cyclic silanes wherein n is 6; m is 12; y is 1; and X is a chlorine atom; or

such halogen substituted cyclic silanes wherein n is 7; m is 14; y is 1; and X is a chlorine atom.

[0039] Additional suitable examples of halogen substituted cyclic silanes include:

such halogen substituted cyclic silanes wherein n is 3; m is 6; y is 1; and X is a bromine atom;

such halogen substituted cyclic silanes wherein n is 5; m is 10; y is 1; and X is a bromine atom;

such halogen substituted cyclic silanes wherein n is 6; m is 12; y is 1; and X is a bromine atom; or

such halogen substituted cyclic silanes wherein n is 7; m is 14; y is 1; and X is a bromine atom.

[0040] Other examples of suitable halogen substituted cyclic silanes include:

chlorocyclopentasilane and/or dichlorocyclopentasilane;

chlorocyclohexasilane and/or dichlorocyclohexasilane;

monochloro- and/or dichloro- derivatives of silylcyclohexasilane;

monochloro- and/or dichloro- derivatives of silylcyclopentasilane;

monochloro- and/or dichloro- derivative of spiro[4.4]nonasilane;

silylcyclopentasilane having 1 and/or 2 chlorine substituents;

spiro[4.4]nonasilane having 1 and/or 2 chlorine substituents;

silylcyclohexasilane having 1 and/or 2 chlorine substituents;

cyclohexasilane having 1 and/or 2 chlorine substituents;

cyclopentasilane having 1 and/or 2 chlorine substituents; and

cyclotrisilane having 1 and/or 2 chlorine substituents.

[0041] Other examples of suitable halogen substituted cyclic silanes include:

bromocyclopentasilane and/or dibromocyclopentasilane;

bromocyclohexasilane and/or dibromocyclohexasilane;

monobromo- and/or dibromo- derivatives of silylcyclohexasilane;

monobromo- and/or dibromo- derivatives of silylcyclopentasilane;

monobromo- and/or dibromo- derivative of spiro[4.4]nonasilane;

silylcyclopentasilane having 1 and/or 2 bromine substituents;

spiro[4.4]nonasilane having 1 and/or 2 bromine substituents;

silylcyclohexasilane having 1 and/or 2 bromine substituents;

cyclohexasilane having 1 and/or 2 bromine substituents;

cyclopentasilane having 1 and/or 2 bromine substituents; and

cyclotrisilane having 1 and/or 2 bromine substituents.

[0042] It will be readily apparent to one skilled in the art that varying substitutions and modifications may be made to the methods and compositions disclosed herein without departing from the scope and spirit of the invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no

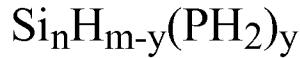
intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention. Thus, it should be understood that although the present invention has been illustrated by specific embodiments and optional features, modification and/or variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0043] In addition, where features or aspects of the invention are described in terms of Markush groups or other grouping of alternatives, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group or other group.

[0044] Also, unless indicated to the contrary, where various numerical values are provided for embodiments, additional embodiments are described by taking any 2 different values as the endpoints of a range. Such ranges are also within the scope of the described invention.

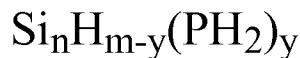
WHAT IS CLAIMED:

1. A doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; and y is an integer from 1 to n.

2. The doped silane of claim 1 wherein said silane is a cyclic compound having the formula:



wherein n is an integer from 3 to 10; m is $2n - 2$ or $2n$; and y is an integer from 1 to n.

3. The doped silane of claim 1 wherein n is an integer from 3 to 10.

4. The doped silane of claim 1 wherein said silane is cyclotrisilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

5. The doped silane of claim 1 wherein said silane is cyclopentasilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

6. The doped silane of claim 1 wherein said silane is cyclohexasilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

7. The doped silane of claim 1 wherein said silane is silylcyclopentasilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

8. The doped silane of claim 1 wherein said silane is silylcyclohexasilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

9. The doped silane of claim 1 wherein said silane is spiro[4.4]nonasilane having 1 or 2 $-\text{PH}_2$ moieties attached thereto.

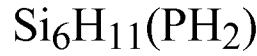
10. The doped silane of claim 1 wherein said silane is a liquid under ambient temperature and pressure conditions (e.g., under 1 atmosphere pressure at 298°C).

11. The doped silane of claim 1 wherein m is $2n$.

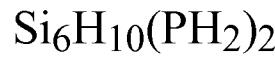
12. The doped silane of claim 1 wherein m is $2n - 2$.

13. The doped silane of claim 1 wherein m is $2n + 2$.

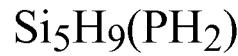
14. The doped silane of claim 1 having the formula:



15. The doped silane of claim 1 having the formula:



16. The doped silane of claim 1 having the formula:



17. The doped silane of claim 1 having the formula:



18. A heteroatom doped silane having a formula:



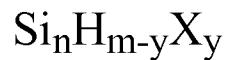
wherein n is an integer from 3 to 10; m is $2n - 2$ or $2n$; and y is 1 or 2.

19. A heteroatom doped silane having a formula:



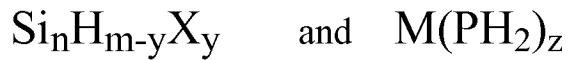
wherein n is an integer from 3 to 7; and y is 1 or 2.

20. A halogen substituted cyclic silane having the formula:

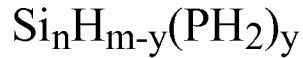


wherein n is an integer greater than 2 (commonly 3 to 10); m is $2n - 2$ or $2n$; y is 1 or 2; and each X independently represents a halogen atom.

21. A method of preparing a doped silane comprising reacting a mixture comprising:



to provide a heteroatom doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; y is an integer from 1 to n; Z is an integer from 1 to 4; each X is independently a halogen atom; and M is a metal atom containing moiety.

22. The method of claim 21 wherein M is an alkali metal.

23. The method of claim 21 wherein $\text{M}(\text{PH}_2)_z$ is:

LiPH_2 , NaPH_2 , KPH_2 , $\text{LiAl}(\text{PH}_2)_4$, or $\text{NaAl}(\text{PH}_2)_4$.

24. A method of preparing a doped silane comprising reacting a mixture comprising:



to provide a heteroatom doped silane having a formula:

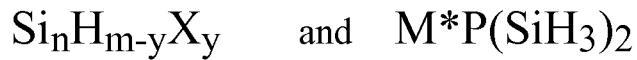


wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; y is an integer from 1 to n; M^* is an alkali metal; R is H or SiH_3 ; and each X independently represents a halogen atom.

25. The method of claim 24 wherein M^*PRSiH_3 is:

LiPHSiH_3 and/or $\text{LiP}(\text{SiH}_3)_2$.

26. A method of preparing a doped silane comprising reacting a mixture comprising:



to provide a heteroatom doped silane having a formula:



wherein n is an integer greater than 2; m is an integer from $2n - 2$ to $2n + 2$; y is an integer from 1 to n; M^* is an alkali metal (e.g., Li); and each X independently represents a halogen atom.

27. The method of claim 26 wherein the halogen atom is a bromine and/or chlorine atom.

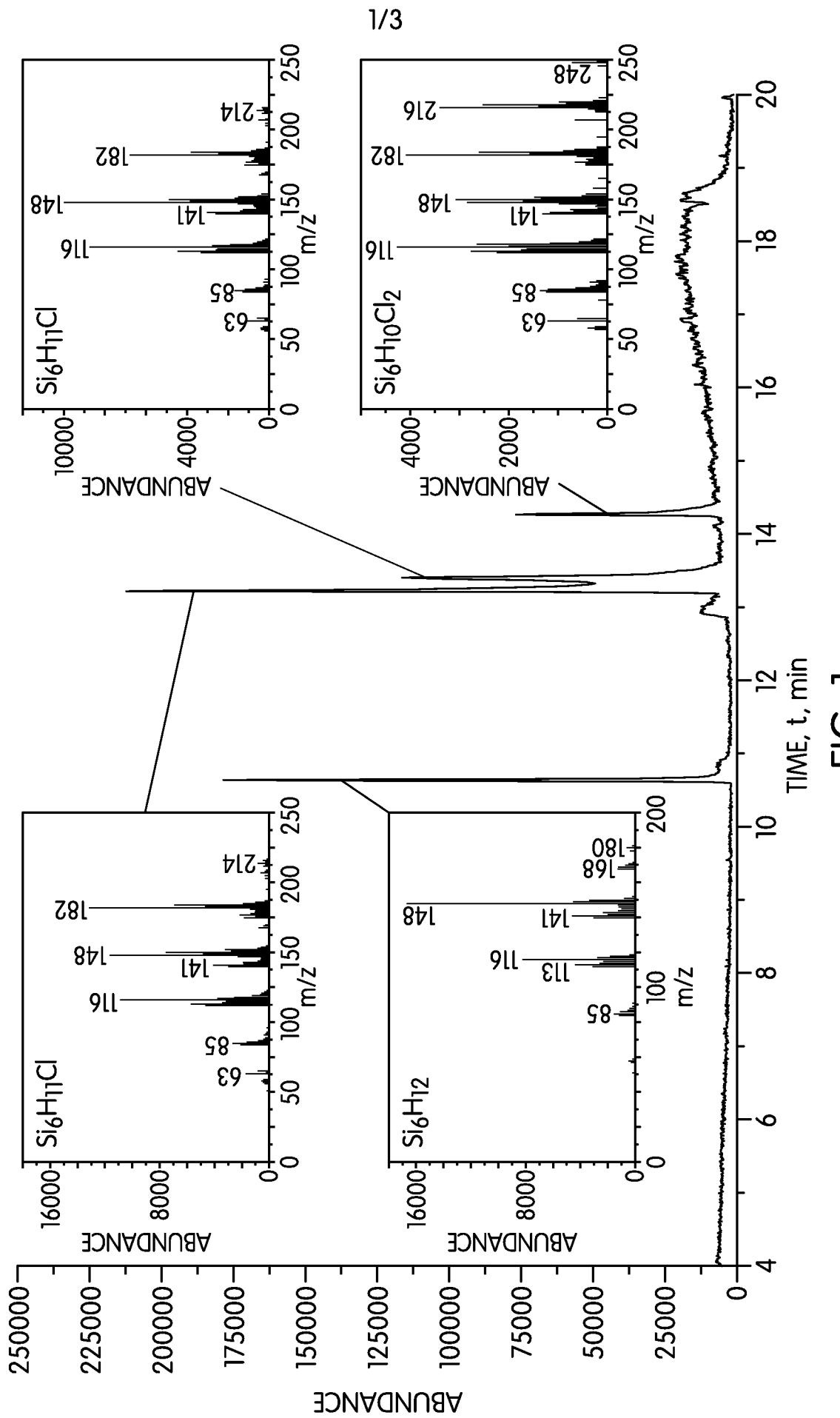


FIG. 1

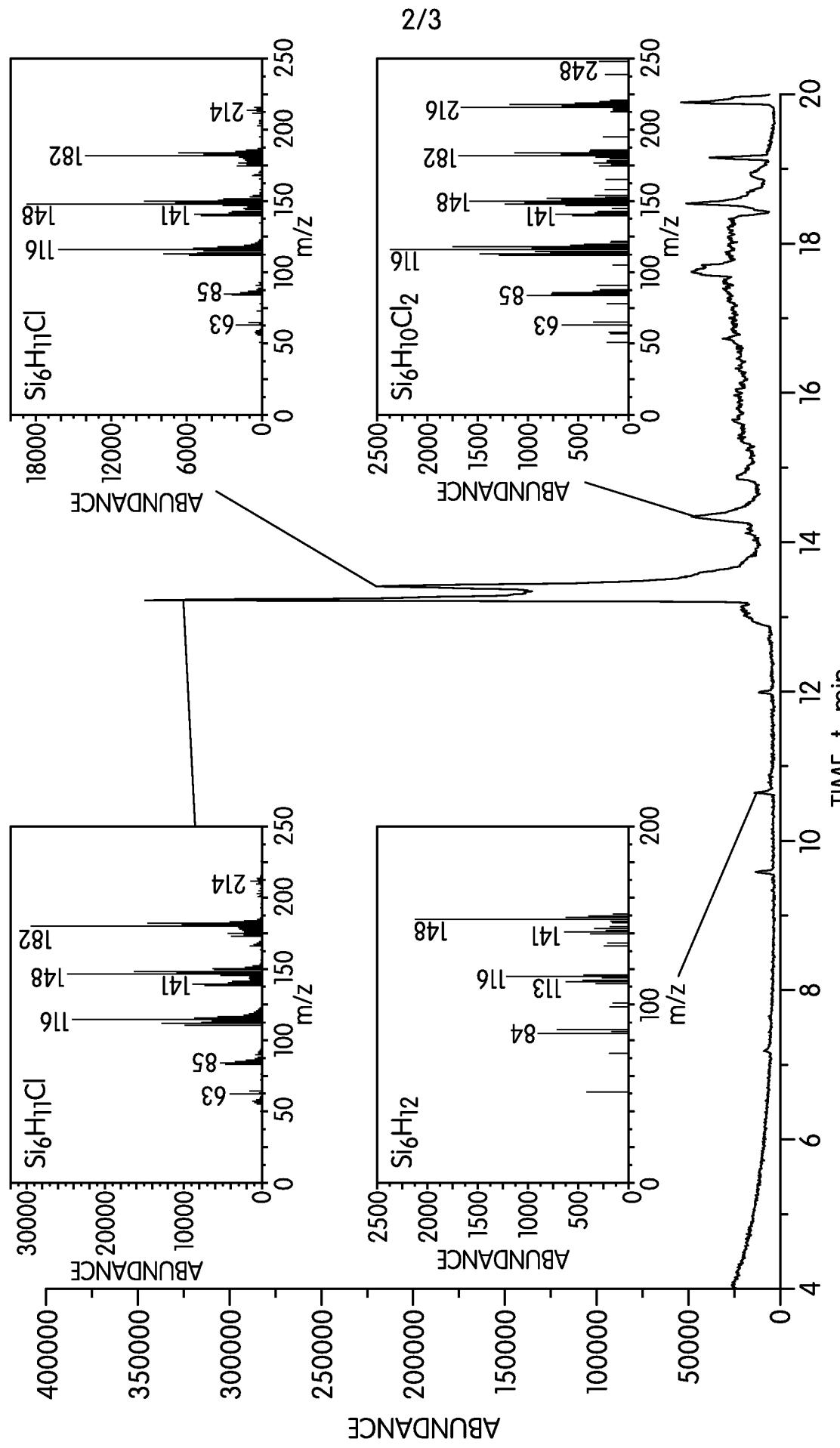


FIG. 2

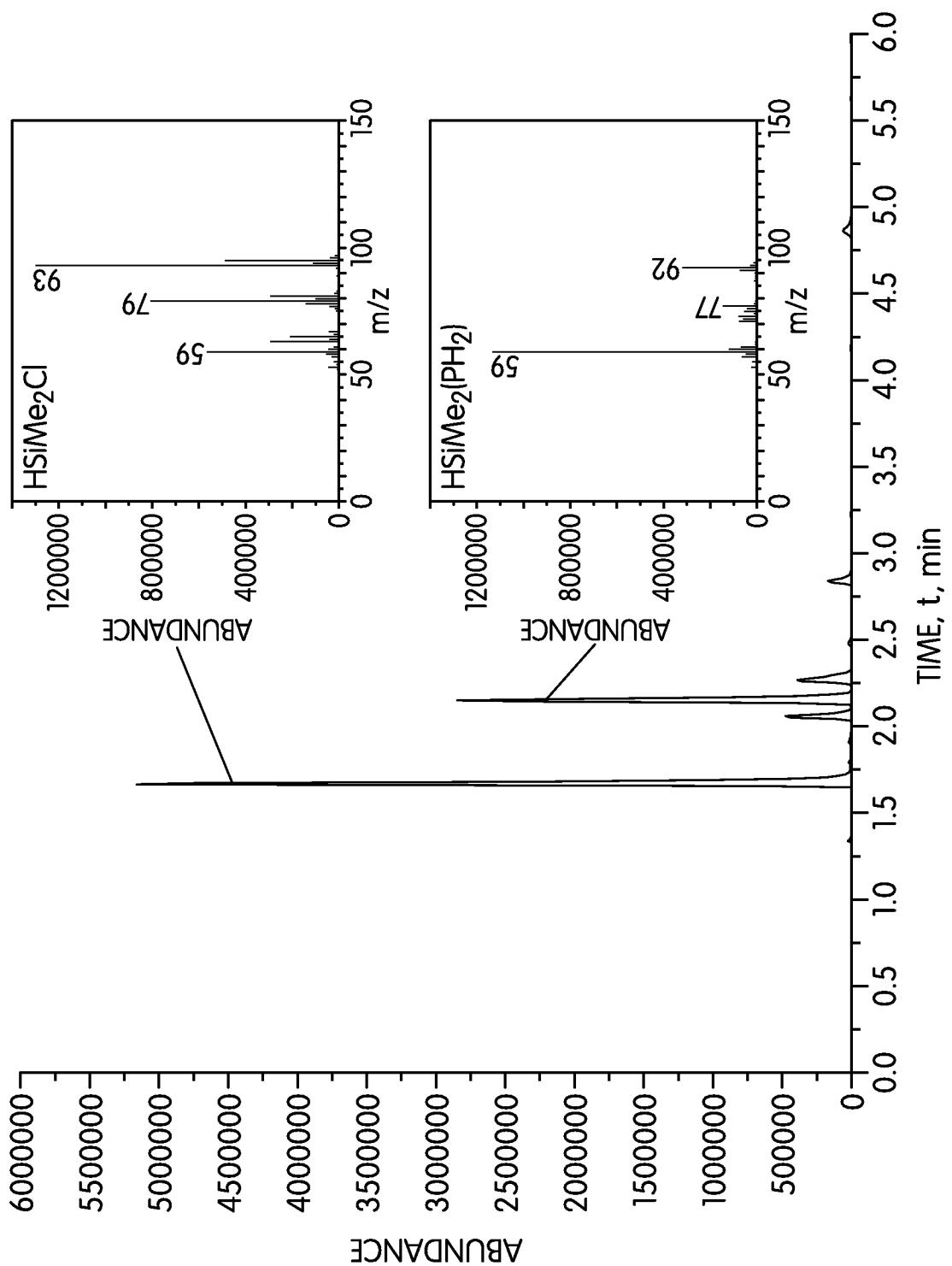


FIG. 3