ALKYL AND ARYL HETEROLEPTIC BISMUTH PRECURSORS FOR BISMUTH OXIDE CONTAINING THIN FILMS

BACKGROUND

[0001] **Field**

[0002] The disclosed and claimed subject matter relates to bismuth precursors of the formula $Bi(R^a)_x(Ar)_{3-x}$ where x = 1 or 2 and the use thereof as precursors for deposition of bismuth-containing films.

[0003] **Related Art**

[0004] Metal-containing films are used in semiconductor and electronics applications. Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have been applied as the main deposition techniques for producing thin films for semiconductor devices. These methods enable the achievement of conformal films (metal, metal oxide, metal nitride, metal silicide, and the like) through chemical reactions of metal-containing compounds (precursors). The chemical reactions occur on surfaces which may include metals, metal oxides, metal nitrides, metal silicides, and other surfaces. In CVD and ALD, the precursor molecule plays a critical role in achieving high quality films with high conformality and low impurities. The temperature of the substrate in CVD and ALD processes is an important consideration in selecting a precursor molecule. Higher substrate temperatures, in the range of 150 to 500 degrees Celsius (°C), promote a higher film growth rate. The preferred precursor molecules must be stable in this temperature range. The preferred precursor is capable of being delivered to the reaction vessel in a liquid phase. Liquid phase delivery of precursors generally provides a more uniform delivery of the precursor to the reaction vessel than solid phase precursors.

[0005] CVD and ALD processes are increasingly used as they have the advantages of enhanced compositional control, high film uniformity, and effective control of doping. Moreover, CVD and ALD processes provide excellent conformal step coverage on highly non-planar geometries associated with modern microelectronic devices.

[0006] CVD is a chemical process whereby precursors are used to form a thin film on a substrate surface. In a typical CVD process, the precursors are passed over the surface of a substrate (*e.g.,* a wafer) in a low pressure or ambient pressure reaction chamber. The precursors react and/or decompose on the substrate surface creating a thin film of deposited material. Plasma can be used to assist in reaction of a precursor or for improvement of material properties. Volatile

CLAIMS

What is claimed is:

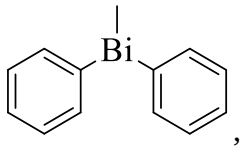
1. A precursor of the formula $Bi(R^a)_x(Ar)_{3-x}$ wherein

(i) x = 1 or 2,

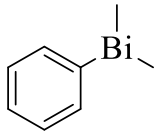
(ii) each R^a is independently one of an unsubstituted linear C_1-C_6 alkyl group, a linear C_1-C_6 alkyl group substituted with one or more halogen, a linear C_1-C_6 alkyl group substituted with an amino group, an unsubstituted branched C_3-C_6 alkyl group, a branched C_3-C_6 alkyl group substituted with one or more halogen, a branched C_3-C_6 alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, and $-Si(CH_3)_3$ and

(iii) each Ar is independently one of a C_3-C_8 unsubstituted aromatic group, a C_3-C_8 aromatic group substituted with one or more halogen, a C_3-C_8 aromatic group substituted with an amino group, a 5-member heterocyclic ring and 6-member heterocyclic ring; and

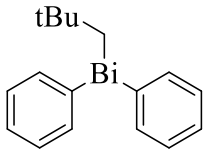
(iv) the precursor does not include:

a. 

,

b. 

; and

c. 

.

2. The precursor of claim 1, wherein R^a comprises an unsubstituted linear C_1-C_6 alkyl group.

3. The precursor of claim 1, wherein R^a is a substituted linear C_1-C_6 alkyl group substituted with an amino group.

4. The precursor of claim 1, wherein R^a comprises an unsubstituted branched C_3-C_6 alkyl group.

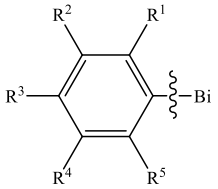
5. The precursor of claim 1, wherein R^a comprises a substituted branched C_3-C_6 alkyl group substituted with an amino group.

6. The precursor of claim 1, wherein R^a comprises an unsubstituted amine.

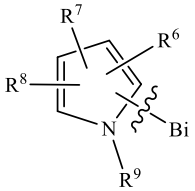
7. The precursor of claim 1, wherein R^a comprises a substituted amine.

8. The precursor of claim 1, wherein R^a comprises one or more of a methyl group, an ethyl group, a propyl group, an n-butyl group, an n-pentyl group, an iso-propyl group, an iso-butyl group, an iso-pentyl group, a sec-butyl group, a sec-pentyl group, a tert-butyl group and a tert-pentyl group.

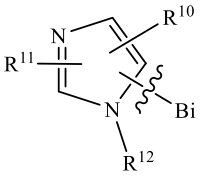
9. The precursor of claim 1, wherein each Ar independently comprises one of:



Ar^1



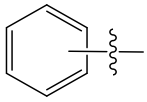
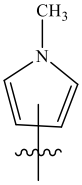
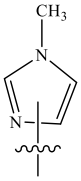
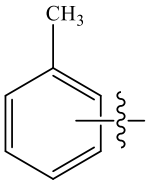
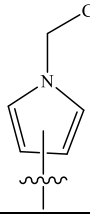
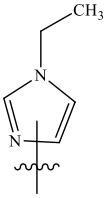
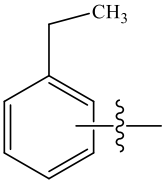
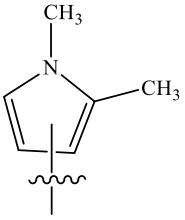
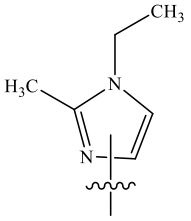
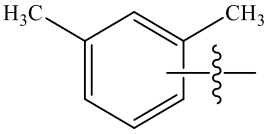
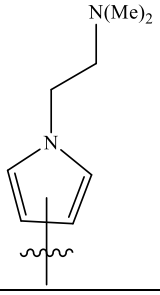
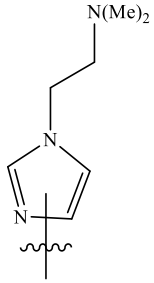
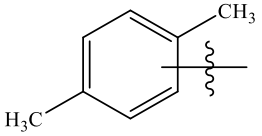
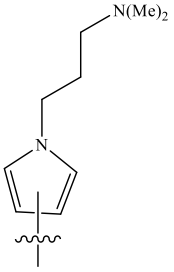
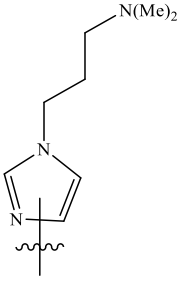
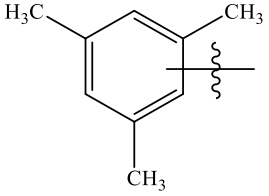
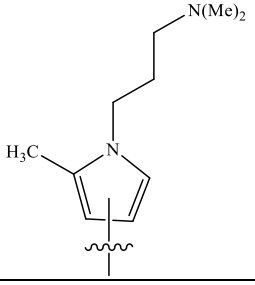
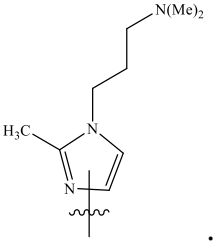
Ar^2



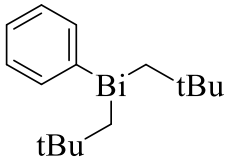
Ar^3

wherein each of R^1-R^{12} is independently H or R^a, wherein R^a is defined as in claim 1.

10. The precursor of claim 1, wherein each Ar independently comprises one of:

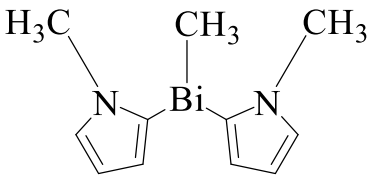
Aryl - Ar^1	**Pyrrolyl - Ar^2**	**Imidazolyl - Ar^3**
		
		
		
		
		
		

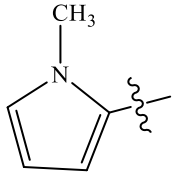
11. The precursor of claim 1 having the structure:



wherein x = 2, each Ra is a neo-pentyl group and Ar is a phenyl group.

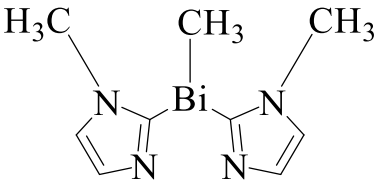
12. The precursor of claim 1 having the structure:

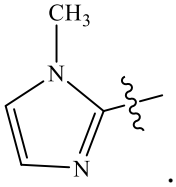


wherein x = 1, Ra is a methyl group and each Ar is 

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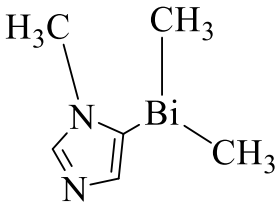
13. The precursor of claim 1 having the structure:

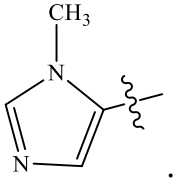


wherein x = 1, each Ra is a methyl group and each Ar is 

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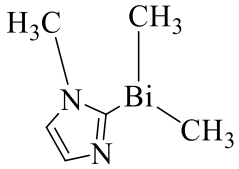
14. The precursor of claim 1 having the structure:

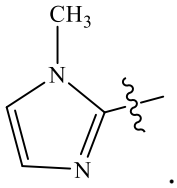


wherein x = 2, each Ra is a methyl group and each Ar is 

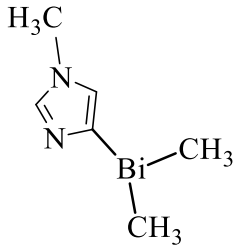
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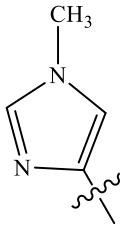
15. The precursor of claim 1 having the structure:



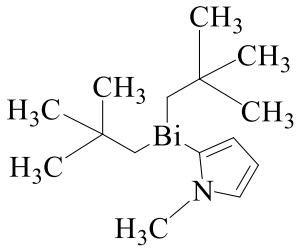
wherein x = 2, each Ra is a methyl group and each Ar is .

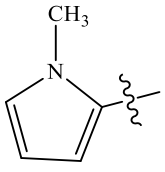
16. The precursor of claim 1 having the structure:



wherein x = 2, each Ra is a methyl group and each Ar is .

17. The precursor of claim 1 having the structure:



wherein x = 2, each Ra is a neo-pentyl group and Ar is .

18. A method for forming a bismuth-containing film on at least one surface of a substrate comprising:

a. providing the substrate with the at least one surface in a reaction vessel;

b. forming a bismuth-containing film on the at least one surface by an atomic layer deposition (ALD) process using one or more heteroleptic bismuth precursor of formula $Bi(R^a)_x(Ar)_{3-x}$ wherein

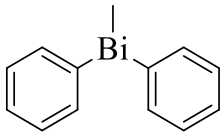
(i) x = 1 or 2,

(ii) each R^a is independently one of an unsubstituted linear C_1-C_6 alkyl group, a linear C_1-C_6 alkyl group substituted with one or more halogen, a linear C_1-C_6 alkyl group substituted with an amino group, an unsubstituted branched C_3-C_6 alkyl group, a branched C_3-C_6 alkyl group substituted with one or more halogen, a branched C_3-C_6 alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, and $-Si(CH_3)_3$ and

(iii) each Ar is independently one of a C_3-C_8 unsubstituted aromatic group, a C_3-C_8 aromatic group substituted with one or more halogen, a C_3-C_8 aromatic group substituted with an amino group, a 5-member heterocyclic ring and 6-member heterocyclic ring.

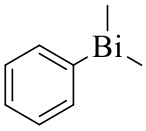
19. The method of claim 18, wherein the heteroleptic bismuth precursor comprises one or more of $BiPhNp_2$, $BiPyr_2Me$, $BiPyrNp_2$, $BiImid_2Me$ and $BiImidMe_2$.

20. The method of claim 18, wherein the heteroleptic bismuth precursor comprises a heteroleptic bismuth precursor of formula $Bi(R^a)_x(Ar)_{3-x}$ wherein x =1, R^a is a methyl group and each Ar is a phenyl group ("$BiPh_2Me$"):



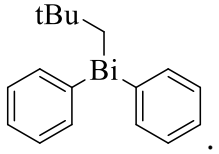
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21. The method of claim 18, wherein the heteroleptic bismuth precursor comprises a heteroleptic bismuth precursor of formula $Bi(R^a)_x(Ar)_{3-x}$ wherein x =2, each R^a is a methyl group and Ar is a phenyl group ("$BiPhMe_2$"):



.

22. The method of claim 18, wherein the heteroleptic bismuth precursor comprises a heteroleptic bismuth precursor of formula $Bi(R^a)_x(Ar)_{3-x}$ wherein x =1, Ra is a neo-pentyl group and each Ar is a phenyl group ("$BiPh_2Np$"):



23. The method of claim 18, wherein the method comprises:

a. providing a substrate in a reaction vessel;

b. introducing into the reaction vessel one or more heteroleptic bismuth precursor of formula $Bi(R^a)_x(Ar)_{3-x}$ wherein

(i) x = 1 or 2,

(ii) each R^a is independently one of an unsubstituted linear C_1-C_6 alkyl group, a linear C_1-C_6 alkyl group substituted with one or more halogen, a linear C_1-C_6 alkyl group substituted with an amino group, an unsubstituted branched C_3-C_6 alkyl group, a branched C_3-C_6 alkyl group substituted with one or more halogen, a branched C_3-C_6 alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, and $-Si(CH_3)_3$ and

(iii) each Ar is independently one of a C_3-C_8 unsubstituted aromatic group, a C_3-C_8 aromatic group substituted with one or more halogen, a C_3-C_8 aromatic group substituted with an amino group, a 5-member heterocyclic ring and 6-member heterocyclic ring;

c. purging the reaction vessel with a first purge gas;

d. introducing into the reaction vessel a source gas;

e. purging the reaction vessel with a second purge gas;

f. sequentially repeating steps b through e until a desired thickness of the bismuth-containing film is obtained.