High-Purity Organosilicon Precursors for Plasma Chemical Deposition of Thin Dielectric Coatings

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(Received April 29, 2002)

Abstract

Ecologically safe methods of obtaining high-purity liquid organosilicon compounds containing Si–O–Si, Si–O–B, Si–O–P, Si–O–Sb, Si–N–Si, Si–N–N bonds are developed. Promising character of their application as precursors for plasma chemical deposition of thin dielectric coatings for different functional applications in the production of integrated circuits and semiconductor devices is shown. New precursors allow one to exclude toxic, flammable, explosive and expensive gases which are used at present, like silane, diborane, phosphine and unstable trimethylstibine.

INTRODUCTION

Technological processes involving deposition of thin coatings for diverse functional destinations (conductive, doping, protective, *etc.*) on surfaces of metals, semiconductors and dielectrics are the basis for the production of modern integrated circuits and other devices for microelectronics. In traditional processes of energy-stimulated deposition of silicon-containing thin dielectric layers (silicon dioxide, including that doped with boron, phosphorus, arsenic, antimony and other elements, silicon nitride and oxynitride), precursors are usually extremely toxic, flammable, explosive expensive gases, such as silane, diborane, phosphine, arsine, *etc.*

We proved that these hazardous and technologically unfavourable reagents can be replaced with high-purity organosilicon compounds, which are non-toxic, safe for production, transportation and lengthy storage, and an order of magnitude cheaper. Principal advantage of the new reagents, which are liquids with boiling points within the range 80–250 °C, over the indicated gases is the presence of ready structural fragments of the layers to be deposited in the new reagents: Si–O–M (M = B, P, Sb, Si), Si–N–Si and Si–N–N bonds.

Under decomposition in the plasma of high-frequency (HF) electric discharge, they form thin dielectric and doping coatings on the surface of crystalline silicon, gallium arsenide, indium antimonide and other materials; in their physicochemical properties these coatings correspond to the structures which are necessary for the production of modern integrated circuits and semiconductor devices. In the present paper we discuss the methods of obtaining most promising high-purity organosilicon precursors the production of which has been established on pilot scale in the Favorskiy Irkutsk Institute of Chemistry, SB RAS, and FGUP "IREA" (Moscow). We also consider the methods of plasma chemical obtaining thin dielectric coatings for various functions developed on the basis of these precursors.

PRECURSORS OF SILICON DIOXIDE FILMS

Highly efficient precursors for plasma chemical deposition of silicon dioxide thin layers are tetramethyldisiloxane (I) and hexamethyldisiloxane (II) which contain structural fragments of silica and silicates −Si−O−Si. They are obtained with quantitative yield by means of hydrolysis of dimethyl- or trimethyltrichlorosilane according to the schemes [1]:

$$2(CH_3)_2HSiCl + H_2O \rightarrow \underset{(I)}{(CH_3)_2HSiOSiH(CH_3)_2} + 2HCl \quad (1)$$

$$2(CH_3)_3SiCl + H_2O \rightarrow \underset{(II)}{(CH_3)_3SiOSi(CH_3)_3} + 2HCl \quad (2)$$

Hexamethyldisiloxane is also formed as a result of hydrolysis of other trimethylsilane derivatives with the general formula $(CH_3)_3SiX$ (where X = OR, SR, NR_2; R = alkyl, aryl, $(CH_3)_3Si$, acyl), which can be used in utilizing wastes from the production of these compounds.

Possessing high volatility and low boiling point (80 and 100 °C), (I) and (II) are purified till the specially pure reagent grade (content of alkaline metal impurities is 10^{-5} % mass, heavy metals − 10^{-6} %) by usual rectification on glass or special steel columns under atmospheric pressure [2].

With UVP-2 and UVP-2M industrial installations, by means of decomposition of vapour-gas mixture (I) or (II) with oxygen in a hf-discharge at the temperature within 150−300 °C, silicon dioxide layers were obtained; their refractive index was 1.460−1.465, efficient charge density (Q_{SS}) from 1 10^{-8} to 8 10^{-8} C/cm^2 [3]. Etching rate in the etching reagent of NH_4F − CH_3COOH − HF − H_2O varied from 0.14 to 0.30 mm/min, porosity from 10 to 20−25 pores/cm^2. The obtained layers have good adhesion to silicon substrates, are distinguished by high mechanical strength and by absence of cracking after thermal treatment at 500 °C. The IR absorption spectra of the films contain bands in the regions: 1085−1065, 825-820, 460−450 cm^{-1}, which are characteristic of amorphous silicon dioxide.

PRECURSORS OF DOPED SILICON DIOXIDE FILMS

On the basis of hexamethyldisiloxane and phosphoric anhydride, a method was developed to obtain silicon- and phosphorus-containing precursor, tris(trimethylsilyl)phosphate (III), containing the structural fragment of phosphorosilicate glass −Si−O−P. The reaction proceeds according to scheme [4, 5]

$$3(CH_3)_3SiOSi(CH_3)_3 + P_2O_5 \rightarrow 2\underset{(III)}{[(CH_3)_3SiO]_3PO} \quad (3)$$

Using specially dried reagents without catalysts, one can obtain yield not more than 25 % [6]; it increases to 88 % in the presence of catalytic amount of water, phosphoric or sulphuric acid. An excess of phosphoric anhydride leads to the formation of a polymer, which is transformed into (II) under heating with additional amount of hexamethyldisiloxane [4]. The compound (III) can be easily purified from admixtures till the especially pure reagent grade by distillation in vacuum.

Silicon- and phosphorus-containing precursors (IV) and (V) with increased phosphorus content were obtained by reaction of hexamethyldisilazane with phosphoric acid with the 85 % yield according to the schemes

$$(CH_3)_3SiNHSi(CH_3)_3 + H_3PO_4 \rightarrow \underset{(IV)}{[(CH_3)_3SiO]_2POH} + NH_3 \quad (4)$$

$$(CH_3)_3SiNHSi(CH_3)_3 + 2(CH_3O)_2POH \rightarrow \underset{(V)}{2(CH_3)_3SiOP(OCH_3)_2} + NH_3 \quad (5)$$

Silicon to phosphorus atomic ratio in tris(trimethylsilyl)phosphite (III), bis(trimethylsilyl)phosphite (IV) and trimethylsilyldimethylphosphite (V) is 3 : 1, 2 : 1, 1 : 1, respectively, which allows one to deposit the films of phosphorosilicate glass with phosphorus mass ratio 1−2 to 14 % under decomposition in the plasma of hf-discharge [7−9]. Coatings obtained from these precursors after thermal treatment at 1000−1100 °C are unlimited source of doping component in doping process, with relatively short diffusion time.

Under heating hexamethyldisilazane with powdered boric acid, tris(trimethylsilyl)borate (VI) containing Si–O–B fragment is obtained with the yield of 70 % [10]:

$$3(CH_3)_3SiNHSi(CH_3)_3 + 2H_3BO_3 \rightarrow \underset{(VI)}{2[(CH_3)_3SiO]_3B} + 3NH_3 \quad (6)$$

On the basis of (VI), a method was developed to deposit thin layers of borosilicate glass with boron mass fraction up to 14.5 % [11]. Diffusion of boron atoms from the films of borosilicate glass (BSG) into silicon plates of KEF-0.5 type at 1050 °C occurs slowly, so they can serve as unlimited source of boron atoms for silicon doping.

With hexamethyldisiloxane and antimony trichloride as initial reagents, a single-reactor method of synthesis was developed to obtain silicon- and antimony-containing organic compound tris(trimethylsilyl)antimonite (VII) with the yield up to 70 % according to the schemes [12]

$$(CH_3)_3SiOSi(CH_3)_3 + C_6H_5Li \rightarrow (CH_3)_3SiOLi + (CH_3)_3SiC_6H_5 \quad (7)$$

$$3(CH_3)_3SiOLi + SbCl_3 \rightarrow \underset{(VII)}{[(CH_3)_3SiO]_3Sb} + 3LiCl \quad (8)$$

The process includes preparation of the solution of phenyllithium in benzene followed by addition of hexamethyldisiloxane and antimony trichloride. Compound (VII) is isolated by usual distillation in vacuum. A side product of the reaction, trimethylphenylsilane, formed with quantitative yield, contains a labile Si–P bond and is a valuable reagent for organic and hetero-organic synthesis.

The SiO_2 films with Sb mass fraction up to 15 % are deposited by the decomposition of (VII) in the hf-discharge plasma. With the rise of substrate temperature from 50 to 150 °C, film deposition rate and antimony content of the film increase from 0.5 to 0.7 mm/h and from 12 to 15 %, respectively. The resulting coatings obtained by plasma chemical method are applied to make n^+-latent layers in silicon semiconductor devices. The SiO_2 layers doped with antimony have minimal defect content and allow forming more perfect epitaxial structures. For example, epitaxial layers with n-type conductivity, grown on silicon substrates, with the parameters of n^+-latent layer ρ_S = 15–30 Ω/• and X_j = 2–5 μm have the following defect-related characteristics: density of packing defects, 10^2 cm^2; density of dislocations, 0–10^2 cm^2; density of traces of crystals (size 10 μm), 0–10^2 cm^2.

PRECURSORS OF SILICON NITRIDE, OXYNITRIDE AND CARBONITRIDE

To obtain silicon nitride and carbonitride, especially pure organosilicon compounds were synthesized, containing Si–N–Si and Si–N–N fragments. The main route of the formation of Si–N bond is the reaction of organic chlorosilanes with ammonia and amines. In the interaction of trimethylchlorosilane with ammonia, instead of the expected trimethylaminosilane (VIII), hexamethyldisilazane (IX) was obtained:

$$2(CH_3)_3SiCl + NH_3 \rightarrow \underset{(VIII)}{(CH_3)_3SiNH_2} + NH_4Cl \quad (9)$$

$$2(CH_3)_3SiNH_2 \rightarrow \underset{(IX)}{(CH_3)_3SiNHSi(CH_3)_3} + NH_3 \quad (10)$$

Similarly, tetramethyldisilazane $(CH_3)_2HSiNHSiH(CH_3)_2$ (X) is formed from dimethylchlorosilane; it differs from (IX) by higher volatility and decreased carbon content. The reaction of dimethyldichlorosilane with ammonia, depending on reaction conditions, leads to cyclic products or to oligodimethylsiloxanes. After addition of dimethyldichlorosilane to liquid ammonia followed by extraction of the reaction mixture with benzene, liquid hexamethylcyclotrisilazane (XI) and solid octamethylcyclotetrasilazane (XII) are formed:

$$(CH_3)_2SiCl_2 + NH_3 \rightarrow \underset{(XI)}{[(CH_3)_2SiNH]_3} + \underset{(XII)}{[(CH_3)_2SiNH]_4} + NH_4Cl \quad (11)$$

Starting from (IX), (X) and (XI), we developed efficient technological processes of plasma chemical deposition of thin coatings com-

$$CH_3)_3SiCl + 2\ H_2NN(CH_3)_2 \rightarrow (CH_3)_3SiNHN(CH_3)_2 + [H_2NN^+(CH_3)_2H]Cl^- \quad (12)$$
(XIII)

$$(CH_3)_2HSiCl + 2\ H_2NN(CH_3)_2 \rightarrow (CH_3)2HSiNHN(CH_3)_2 + [H_2NN^+(CH_3)_2H]Cl \quad (13)$$
(XIV)

$$(CH_3)HSiCl_2 + 4\ H_2NN(CH_3)_2 \rightarrow (CH_3)HSi[NHN(CH_3)_2] + 2[H_2NN^+(CH_3)_2H]Cl \quad (14)$$
(XV)

posed of silicon nitride and oxynitride [14–16]. For instance, we obtained silicon nitride layers on the surface of silicon substrates in the low-pressure hf-plasma (1–5) 10^{-2} mm Hg) from a mixture of hexamethyldisilazane (IX) and nitrogen. The substrate temperature does not exceed 200 °C, the deposition rate is 1.2–2.0 μm/h, the refractive index N_D = 1.9–2.5, depending on (IX) to N_2 ratio in the initial vapour and gas mixture. The dielectric rigidity of the coatings is (9–20) 10^6 V/cm, the porosity of Si_3N_4 films is 2–10 pores/cm^2. Films of weakly nitrogenated silicon oxynitride are deposited from the gaseous mixture of (IX) and O_2.

Processes developed on the basis of these reagents allow obtaining protective, insulating and passivating coatings for the production of integrated circuits and semiconductor devices.

New precursors containing Si–N–N fragments, for use in plasma chemical deposition of nitrogen- and silicon-containing coatings, are trimethyl(2,2-dimethylhydrazino)silane $(CH_3)_3SiNHN(CH_3)_2$ (XIII), dimethylsilyl(2,2-dimethylhydrazino)silane $(CH_3)_2HSiNHN(CH_3)_2$ (XIV) and methyl-bis-(2,2-dimethylhydrazino)silane $(CH_3)HSi[NHN(CH_3)_2]_2$ (XV). Compounds (XIII) and (XIV) were synthesized with the yield of up to 90 % according to the reaction of the corresponding chlorosilanes with 1,1-dimethylhydrazine [17] (schemes (12)–(14)).

Depending on the chemical composition of reaction mixture and reactor type, coatings of different chemical composition are formed during decomposition in the plasma of hf-discharge. For example, in the UVP-2M installation at 1150–300 °C, vapour and gas mixture composed of (XIII) or (XIV) and oxygen leads to the deposition of SiO_2 films; silicon nitride layers are deposited from a mixture of (XIII) or (XIV) with ammonia or nitrogen; ternary mixture (XIII) or (XIV) + oxygen + trimethylsilyldimethylphosphite (V) gives deposition of phosphorosilicate glass [17].

Thin films of silicon carbonitride were obtained on the basis of (XIII) and (XIV) using chemical vapour deposition in the remove plasma hf-discharge in the atmosphere of helium or hydrogen [18]. By means of electron microscopic investigation of these layers, it was established that silicon carbonitride nanocrystals of 50–200 nm in size are present in the amorphous matrix. The resulting coatings are thermally stable till 1000 °C.

CONCLUSION

Waste-free, ecologically safe methods for obtaining high-purity organosilicon precursors for plasma chemical deposition of dielectric coatings for use in microelectronic technology were developed on the basis of commercial products: methylchlorosilanes, ammonia, antimony trichloride, *etc*. These precursors replace presently used flammable, explosive, toxic and expensive reagents: silane, diborane, phosphine, trimethylstibine, and allow substantial improvement of safety, technical and economic indices of production.

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