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Trimethyl(phenyl)silane — a Precursor for Gas Phase Processes of SiC\textsubscript{x}:H Film Deposition: Synthesis and Characterization

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Abstract. The technique of synthesis and purification of trimethyl(phenyl)silane PhSiMe\textsubscript{3}, allowing to obtain the product with high yield. Individuality of the product was confirmed by elemental analysis for C, H, Si, IR, UV and \textsuperscript{1}H NMR-spectroscopic studies, defined its spectral characteristics. Complex thermal analysis and thermogravimetric defined thermoanalytical behavior effects of PhSiMe\textsubscript{3} in an inert atmosphere. Tensimetric studies have shown that the compound has sufficient volatility and thermal stability for use as a precursor in the process of chemical vapor deposition (CVD). The composition and temperature limits of the possible crystalline phase complexes in equilibrium with the gas phase of different composition has been determined by method of thermodynamic modeling. Calculated CVD diagrams allow us to select the optimum conditions of film deposition. The possibility of using trimethyl(phenyl)silane in CVD processes for producing dielectric films of hydrogenated silicon carbide has been demonstrated.

Key words: trimethyl(phenyl)silane, PECVD, dielectric films, hydrogenated silicon carbonitride.

Introduction

The challenge of creating new materials requires an extended range of precursors used in the chemical vapor deposition (CVD) processes, whose nature is critical for the formation of films with the desired properties. Organic element / silicon compounds are considered to be promising materials for the synthesis of Si—C—N—H films. The advantage of these substances is aggregation combination of physicochemical characteristics necessary for the implementation of CVD processes as well as their presence in the molecules of the ready fragments for the formation of films with the desired chemical composition. The use of these substances will provide for a substantial simplification of manufacturing processes. Thin films on the basis of hydrogenated silicon carbide SiC\textsubscript{x}:H attract the attention of researchers as these possess a number of critical fundamental characteristics: high transparency in the visible spectrum [1], high hardness and Young’s modulus [2] along with a low dielectric constant [3]. SiC\textsubscript{x}:H films can be used as anti-reflective and passivating coatings for solar cells [4]. It should be noted that their functional characteristics change depending on the carbon and hydrogen content. For SiC\textsubscript{x}:H film synthesis, various organosilicon compounds are used such as dimethyl- and trimethylsilanes [5], diethylsilane [6], bis(dimethylsilyl)ethane [7] and tetravinylsilane [2]. The effect of the structure and Si:C ratio in the precursor molecule on the properties of SiC\textsubscript{x}:H films have been the subject of investigations. A search for new precursors for CVD processes is still underway. The substances used in the said processes should meet to the following requirements:

- sufficient volatility providing for the formation of films with a certain growth rate within the desired temperature range;
- thermal resistance to decomposition during evaporation or sublimation;
- substantial temperature difference between evaporation and decomposition for film synthesis;
- high chemical purity;
- decomposition of precursors without forming solid by-products;
- long-term shelf life;
- low cost;
- low hazard degree [8].

For the enhancement of SiC\textsubscript{x}:H film functionality, the challenging task of looking for new film-forming precursors along with the development of low-temperature film synthesis processes on their basis is still outstanding. The aim of this work is to synthesize and characterize trimethyl(phenyl)silane (PhSiMe\textsubscript{3}) and to study its possible use as a reactant in the formation of SiC\textsubscript{x}:H films by plasma-enhanced chemical vapor deposition (PECVD).

Samples and Research Techniques

Trimethyl(phenyl)silane was obtained through trimethylchlorosilane phenylation as follows:
Me₅SiCl + PhMgBr → PhSiMe₅ + MgBrCl,

where Ph = (C₆H₅) and Me₅ = (CH₃)₅. The target product PhSiMe₅ was obtained by vacuum distillation through product recovery at T_SCAN = 328 K (2 · 10³ Pa). The content of C, H and Si was determined by combustion and using a C-, H- and N- analyzer (Flash EA 1112 Series ThermoFinnigan). The nuclear magnetic resonance (NMR) spectra were obtained at room temperature on a Bruker DPX400 spectrometer (400.13 MHz —¹H; 100.58 MHz —¹³C; 79.46 MHz —²⁹Si). The solvent was CDC1₃, in-house standard — tetramethylsilane. The IR spectrum of trimethyl(phenyl)silane placed between KBr glasses and that of the films were obtained using a Digilab Scimitar FTS 2000 FTIR spectrometer operating within the wavenumber range from 375 to 7800 cm⁻¹ at a resolution of 1 cm⁻¹. The UV spectrum of PhSiMe₅ deposited onto optically transparent quartz was obtained on a Shimadzu UV3101PC scanning spectrophotometer in the wavelength range from 190 to 800 nm.

A comprehensive thermal analysis (CTA) was conducted using TG 209 F1 Iris thermo-microbalance (NETZSCH, Germany) in helium within the temperature range from 293 K to 1273 K. The weight measurement accuracy was ±0.1 µm. The sample heating and cooling rate was from 0.001 to 80 K/min. The saturated vapor pressure for the substance was determined by a static tensiometry method with a glass membrane nullmanometer. The measurement error of this method did not exceed 1 torr (1 torr = 133.322 Pa), the temperature maintenance and measurement error being equal to ±0.5 K. The technique was described earlier [9].

SiC₅H₃ films were synthesized by PECVD. Synthesis was conducted with the use of a tunnel-type quartz reactor by the inductive plasma excitation from a UVC-66 oscillator (frequency of 40.68 MHz). The specific power of the HF discharge amounted to 0.17 W/cm². The partial pressure of PhSiMe₅ inside the reactor was equal to 1.5 · 10⁻² torr, and that for helium, 6 · 10⁻³ torr. The film growth zone was placed at 373-673 K in a resistance furnace. The film thickness and refractive index were determined by monochromatic zero ellipsometry using a LEF-3M device (the incident radiation wavelength was λ = 632.8 nm). The film growth rate was calculated as the ratio between film thickness and synthesis time. The combined diffused light (CDL) spectra were obtained on Triplemate Raman spectrometer (Spex, USA) within the wavenumber range of 400-1800 cm⁻¹ (δ = 488 nm). The surface morphology and film elementary composition were studied using a JSM 6700F scanning electron microscope equipped with the EX23000 BU energy dispersive spectroscopy (EDS) system.

The film electrophysical properties were studied by capacitance-voltage (C-V) characterization in the metal-dielectric-semiconductor (MDS) test structures. The capacitance measurement error did not exceed 5%. In order to synthesize such structures we sputtered an aluminum electrode on the SiC₅H₃ film deposited on a silicon substrate. The C-V characteristics of the structures were measured using an automated plant built around E7-12 and E7-14 capacitance bridges. The measuring frequency was varied in the range from 1 kHz to 1 MHz, the amplitude of the HF testing signal being 20 mV. For applying a bias voltage to the sample, a digital-to-analog converter was used complemented with a DC voltage amplifier or an internal measurement bridge source. The measurement procedure was PC controlled. The results were used for the calculation of the dielectric permeability ε.

Results and Discussion

The synthesized PhSiMe₅ was subjected to characterization using a set of techniques providing for the description of the obtained compound properties to the fullest possible extent. NMR spectrum of ¹H, δ, ppm: 0.04 s (¹H, CH₃Si), 7.02-7.65 m (¹H, C₆H₅). NMR spectrum of ¹³C, δ, ppm: 1.10 (CH₂Si), 117.15 (m-CH), 128.13 (p-CH), 133.15 (o-CH), 141.74 (C-Si). According to the NMR spectroscopy data, the PhSiMe₅ purity amounted to at least 99.5%. The elemental analysis showed the following element contents: C — 71.82%; H — 9.16%; Si — 18.62%.

For the C₆H₅Si formula, the calculation results are as follows: C — 71.92%; H — 9.39%; Si — 18.69%. The Beilstein test for halogen was negative. The PhSiMe₅ IR spectrum (Fig. 1) is characterized by the absorption bands corresponding to the Si—C stretching vibrations in monosubstituted trimethylsilyleyl group Si—(CH₃); a strong band at 840 cm⁻¹ and another band at 756-754 cm⁻¹. The compound spectrum also features a band at 1250 cm⁻¹ corresponding to the deformation vibrations of this bond. Furthermore, the IR spectrum of PhSiMe₅ appeared to contain some bands of medium and strong intensity that are typical of the Si—C₅H₃ bond that have the following frequencies: 1427, 1114, 727 and 696 cm⁻¹ [10, 11]. It should be noted that along with the above, the spectrum features some bands conditioned by the ν (≡C≡C—) stretching vibrations in the benzene ring within the 1650-1510 cm⁻¹ range that correspond to deformation vibrations at 620 and 465 cm⁻¹ [12, 13]. The 3069-2900 cm⁻¹ range contained two groups of bands caused by the antisymmetric and symmetric C—H stretching vibrations both in the benzene ring (3070-3018 cm⁻¹) and in the methyl groups (2957-2897 cm⁻¹). In this case, the intensity of the latter bands was much higher. The in-plane and out-of-plane C—H deformation vibrations in the benzene ring manifest themselves in the 1000-1250 and 900-720 cm⁻¹ ranges, respectively. This compound was subjected to UV spectroscopy and the region of its spectral response to UV radiation (200-310 nm) was determined. A distinctive feature of the UV spectrum of this substance (Fig. 2) is the 265 to 310 nm range, which is responsible for the π-π* transitions within the benzene ring.

In order to select the conditions for chemical vapor deposition, data on the dependence of the saturated vapor pressure on temperature and thermal stability of the volatile film-forming precursors are required. Comprehensive thermal analysis (CTA) holds a specific place amongst the physicochemical research techniques used for this purpose as it is essentially a rapid method providing quick and high-quality information on the chemical and physicochemical processes progressing in the substance under programmed temperature variations. Figure 3 presents the results of PhSiMe₅ CTA. These data were used as the basis for the identification of temperature ranges of thermoanalytical and thermogravimetric effects of the substance behavior in an inert atmosphere. It was demonstrated that the substance transitions to the gas phase without any decomposition occur in the
The saturated vapor pressure above liquid trimethyl(phenyl)silane was measured by the static technique using the membrane null manometer in the 300-401 K temperature range. The substance is thermally stable within the above temperature range. Processing of the experimental data yielded the temperature dependence of the PhSiMe3 saturated vapor and calculation of thermodynamic parameters of the process of its vaporization: In (p/ atm) = 11.90 - 5270/T; ΔH_vap = 44.0 ± 0.5 kJ/mol, ΔS_vap = 99.0 ± 1.0 J/(mol · K), where p, ΔH_vap, ΔS_vap — PhSiMe3 saturated vapor pressure, evaporation enthalpy and entropy, respectively.

The thermodynamic simulation method was used for the assessment of the phase composition of the deposited layers and the gas phase content under various film deposition conditions (temperature, total pressure and reactant ratio). The results were used for the selection of the conditions for the film CVD process. The calculation of the equilibrium composition of the physicochemical system under these thermodynamic conditions was described in detail earlier [14]. Simulation was conducted using the database and application software for equilibrium calculations from the thermodynamic section of the Data Bank on Properties of Electronic Engineering Materials maintained at the Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences. The values recommended in the reference publication [16] were taken as the basis when selecting the thermodynamic characteristics subject to calculations. The standard thermodynamic characteristics of individual substance

\[ \Delta_f H_{298K}, \Delta_f S_{298K}, C_p = f(T) \]

were used as the initial thermodynamic information. It was assumed that the condensed phases have permanent compositions while the gaseous compounds are governed by the ideal gas law. The calculation of the detailed composition of the physicochemical system under these thermodynamic conditions relies on the Gibbs free energy minimum principle subject to the limitations set by the conditions of the system mass balance maintenance. The calculations considered up to 100 molecular forms of the gas phase and condensed compounds. Unfortunately, there are no thermodynamic characteristics for the ternary silicon carbonitride compounds as yet. The phase composition simulation results for the reactant-hydrogen system are presented as CVD curves in Fig. 4, a. As the total pressure in the reaction chamber increases, the phase boundaries shift towards the region of higher synthesis temperatures. The interval for obtaining the SiC phase is rather narrow and lies within the region of low deposition temperatures. Film deposition without adding carbon is only possible if the reactant is highly diluted with nitrogen. The equilibrium gas phase mainly contained methane and hydrogen (Fig. 5, a). The calculation results for the "PhSiMe3 - inert gas (helium)" system demonstrated that only a mixture of silicon carbide and carbon (SiC + C) should be formed in the 300-1300 K temperature range. The phase composition calculation results for the reactant- ammonia system under a total pressure of 0.01 torr are presented as CVD curves in Fig. 4, b. As the pressure rises, the temperatures that characterize the phase boundaries increase. In this case, the deposition of three phase complexes is predicted, depending on the conditions. At a low ammonia content and low temperatures, joint deposition of three phases is expected: Si3N4 + SiC + C. If the content of ammonia is increased, the region of this phase complex existence narrows abruptly. If the NH3/reactant ratio is 1.3 or more, carbon-doped silicon nitride is deposited in the lower temperature range. At high temperatures, the SiC + C mixture will be deposited. Figure 5 presents the calculated composition of primary gas phase components for the systems with nitrogen, helium and ammonia.

A technique of obtaining thin films of hydrogenated silicon carbide SiCnH from the mixture of trimethyl(phenyl)silane and helium was developed and implemented on the basis of the preliminary calculations and experiments. The film growth rate decreases steadily as the synthesis temperature is increased from 65 to 30 nm/min. It should be noted that the film deposition rate is not high. This provides for an accurate control of the film thickness. The IR and CDL spectroscopy data were used for characterization of the chemical composition of the films. SiC/Hi (100) samples of close thickness (~200 nm) were synthesized to ensure correlation of the results obtained by these techniques. Figure 6 presents IR absorption spectra of SiCnH films synthesized in the 373-673 K temperature range along with the spectrum of the precursor, trimethyl(phenyl)silane. The IR spectra were interpreted on the basis of the data of earlier publications [10-13]. The presence of a wide band in the 700-1000 cm⁻¹ region can be distinguished in the spectra of all films, where peaks correspond to the respective Si—C vibrations (800-794 cm⁻¹), Si—CH3 (840 and 756 cm⁻¹) and Si—CnH4 (730 and 696 cm⁻¹) groups can be expected [5-7]. The spectra also feature a band with a frequency of 1250 cm⁻¹ associated with the Si—CH2 deformation vibrations. No peaks corresponding to the benzene ring deformation vibrations (464 and 619 cm⁻¹) were detected in the film spectra. It should be noted that the film IR spectra obtained at 373-473 K are close to the IR spectrum of the parent molecule of PhSiMe3, which is indicative of the incorporation of single precursor fragments into the film structure. The absorption bands at 696 and 1427 cm⁻¹ corresponding to the Si—CnH4 vibrations disappear from the spectra of the films obtained at temperatures above 473 K. As the synthesis temperature is increased, changes in the remaining portion of the IR spectrum are observed. Some decrease in the intensity of the peaks related to the C—H vibrations was detected. Also interesting is the appearance of absorption bands with frequencies of 1050 and 2100 cm⁻¹ corresponding to the vibrations of Si—CH2—Si and Si—H bonds which were absent in the parent molecule. The presence of these bonds testifies to a deep breakdown of the parent PhSiMe3 molecule.

Combined diffused light (CDL) spectra were obtained in order to determine the presence and state of the elementary carbon phase. It was determined that the films synthesized at temperatures of up to 673 K contain no elementary carbon phases with own CDL spectra. The only maximum observed relates to the vibrations in the silicon substrate lattice.

The elemental composition of silicon carbonitride films was determined by EDS on specially synthesized SiCnH/Ge(110) structures. Since the precursor is represented in the process by an organosilicon compound, the hydrogen contained in the precursor can be found in the film composition, which is proved by the presence of respective peaks in the IR spectra. As EDS cannot be used for determining the film hydrogen content, these data may be considered as qualitative only. Nevertheless, this technique allows pointing out some tendencies in the elemental composition of the films depending on changes in the conditions of their synthesis. It was revealed that the film composition features such elements as Si, C and O and the oxygen content in the
films reaches 5 (at.%)%. The presence of oxygen can be due to several reasons. First, it can be incorporated into the film owing to quartz reactor plasma etching. Secondly, which is more probable for low-temperature polymer-like films, the surface of the synthesized sample absorbs air oxygen and moisture when removed from the reactor upon experiment completion. The content of carbon discovered in the film composition decreases as the synthesis temperature rises but still remains much higher than the content of other elements (Fig. 7). Investigations of the surface morphology by scanning electron microscopy showed that the films have a smooth surface without any peculiarities.

For the investigation of dielectric properties of the films, Al/SiC_x:H/Si (100) MDS test structures were synthesized. The parent gas mixture was TMPS + He. The deposition temperature was varied in the course of synthesis. Presented below are the experimental values of the film dielectric permeability.

<table>
<thead>
<tr>
<th>Deposition Temperature, K</th>
<th>ε</th>
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<tbody>
<tr>
<td>373</td>
<td>3.73</td>
</tr>
<tr>
<td>473</td>
<td>3.35</td>
</tr>
<tr>
<td>573</td>
<td>2.96</td>
</tr>
<tr>
<td>673</td>
<td>3.73</td>
</tr>
</tbody>
</table>

It was discovered that the films obtained within the whole range of the selected conditions possess a low dielectric permeability due to a high content of CH_x groups. The positive effect of hydrocarbon groups, especially methyl ones, on obtaining the films with low ε is well known [17]. The values of ε for the films obtained from PhSiMe_3 correspond to the typical dielectric permeability values for the SiC_x:H films deposited from various precursors [18].

Conclusion

A synthesis and purification technique for the trimethyl(phenyl)silane has been developed, its physicochemical properties have been studied and its possible use as a precursor in the chemical vapor deposition processes has been demonstrated. The optimum deposition conditions for dielectric films of hydrogenated silicon carbide have been determined.

References

230 p.

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Fig. 1. IR Spectrum of Trimethyl(phenyl)silane

Fig. 2. Optical Spectrum of Trimethyl(phenyl)silane

Fig. 3. Data of Comprehensive Thermal Analysis of Trimethyl(phenyl)silane: 1 — Differential Thermal Analysis (DTA); 2 — Thermogravimetry (TG)

Fig. 4. CVD curves: (a) PhSiMe₃ + H₂ base mixture, SiC / SiC + C boundary at various total chamber pressures is shown ((1) 0.001 torr; (2) 0.01; (3) 0.1); (b) PhSiMe₃ + NH₃ Base Mixture (at a Total Reactor Pressure of 0.01 torr)

Fig. 5. Gas Phase Composition Calculated at a Total Chamber Pressure of 0.01 torr for Various Systems: (a) PhSiMe₃ + H₂ (4 : 1); (b) PhSiMe₃ + He (4 : 1); (c) PhSiMe₃ + NH₃ (4 : 1)

Fig. 6. IR Spectra of (1) PhSiMe₃ Precursor and (2—5) Films Synthesized from a Mixture of PhSiMe₃ and Helium under Various Temperatures: (2) T = 373 K; (3) 473; (4) 573; (5) 673

Fig. 7. Element Ratio in SiCx:H Films Deposited from PhSiMe₃ + He Mixture vs. Temperature: the Dotted Line Indicates the C/Si Ratio in the PhSiMe₃ Precursor