THIN FILMS OF SILICON COMPOUNDS DEPOSITED BY FILAMENTARY BARRIER-DISCHARGE

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Abstract

Hexamethyldisilazane (HMDSN) and hexamethyldisiloxane (HMDSO) were used as organosilicon reagents for PECVD of thin films in filamentary barriers at low atmospheric pressure at the frequency of 5 kHz. The films containing SiO and SiN functional units of organosilicon fragments Si-C-H, C-O, and Si-H groups were deposited on Si substrates and examined using FT-IR and XPS spectroscopy, mechanical properties measurement, and AES characterization of the surface.

1. Introduction

Organosilicon compounds such as tetrachlorosilane (TCS), hexamethyldisilazane (HMDSN), hexamethyldisiloxane (HMDSO), etc., are advantageous starting materials so-called precursors for thin film plasma deposition (PECVD) at room temperature such as silicon nitride, etc. (1-3). The main reason lies in the material's unique properties such as chemical and thermal stability, low flammability, and low toxicity. However, the stability and complex structure of organosilicon compounds makes their chemical transformations generally not so easy and rapid as that of silane. In the thin films deposited using TCS, HMDSN, etc., some fragments of the organic structure Si-C-H, Si-O-Si-C-H, etc., were found in a number of experiments. Such residues affect the quality of the films by modifying their resistance to the action of atmospheric agents, hardness and abrasion resistance, refractive index, as well as their porosity and adhesion to the substrate. In the present study, HMDSN and HMDSO were used as organosilicon reagents for plasma deposition of thin films under filamentary DD conditions at atmospheric pressure.

2. Experimental methods

Thin films were produced in DBD reactor (the same as in Ref. 5) with an external high-voltage electrode 370 mm in diameter separated from the discharge space with a quartz glass plate 1 mm thick, the discharge gap distance being about 1.5 mm. Films were deposited on polished single-crystal (100) silicon wafers (thickness of 0.37 mm and area of about 2 cm²) placed directly on the grounded electrode. Substrate temperature was controlled from ambient up to 400°C and the reactor was powered from a circuit operating at about 5 kHz and 21 to 26 kV.

A mixture of gases fed into the reactor was prepared by passing the carrier gas argon or nitrogen through the liquid organosilicon reagent: hexamethyldisilazane (Sigma-Aldrich, NF 15762) and hexamethyldisiloxane (Tokyo Kasei, NF 82620). The gases (N₂, H₂, NO, Ar, N₂O) of commercial grade were purified by passing over solid potassium hydroxide and
chloromethylated absorbent. Oxygen was removed from argon and nitrogen on a copper catalyst.

Film thickness was measured by ellipsometry at 632.8 nm wavelength using a He-Ne laser. 

The FT-IR absorption spectra were recorded using a Bruker IFS 113V spectrometer in the transmission mode.

For XPS analysis, an ESCALAB 210 photoelectron spectrometer (VG Scientific Instruments, UK) was used with AlKα (1486.6 eV) X-ray source.

Film nanomechanical characteristics have been measured by means of an instrument (NanoScope IV, Digital Instruments, USA) capable to make indentations at very low loads (1 to 50 N) and load-displacement measurements with sub-nanometer indentation depth sensitivity.

Characterisation of the surface was made by means of Atomic Force Microscope prototype made in Lódz University, Faculty of Physics.

3. Results

The effect of substrate temperature T was investigated using HMDtrimethylamine (HMTA) and TMCS in the ratio 1:1.5. In a range of 75 to 200°C the presence of organo-inorganic compounds was found in samples H80 and H80-C. These IR spectra showed not only Si-O-Si absorption bands at 1200, 1100, and 800 cm⁻¹, but also strong bands associated with Si-O-C, N-O, C-N, and C=O groups. When the samples were annealed at 300°C, the same absorption bands were identified as arising from Si-O-Si, C=O, and N-O bonds. The content of organic residues content thermally evident is low.

![Fig. 1 Spectra FT-IR of the sample H80](image1)

![Fig. 2 Spectra FT-IR of samples H80, 81, 68](image2)

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The influence of gas mixture composition on the film properties was observed for 1400°C using gases of NH₃-N₂ mol ratio up to 1 sample H25, P01, H09, H10, and H15. The main absorption bands in 3621, 3543, 3320, 1636 cm⁻¹ were recorded for NH₃ gas; other absorption bands may be assigned to NH₂ groups, stretching (NH₃) N-H the strong bands of amide B from H₂NCOH in H25 and H09 and with other bands being assigned to NH3-NH and N-N. The XPS spectra of the films grown from ammonia at gas mixture NH₃-N₂ show evidence of considerable nitrogen concentrations: 8 at. % for the sample H25 and 20 at. % for H09. Measurements of the microhardness and elastic modulus of films H25 (H1), H3, and different contact depths have shown the presence of thin surfaces layer about 30 nm which was found rather soft (20-30 GPa) with the deeper zone of hardness up to 120 GPa which is almost as high as that of sintered carbide (140 GPa). Also the elastic modulus in the deeper zone is about the same close to that of sintered steel (210 GPa) respectively.

Fig. 1: Hardness of the sample H25.
In the next experiment, HMDSO was used as a monomer during sputtering. In the film grown from HMDSO, NCO-A mixture at 100°C, (with no amorphous structure) were found, thus...

This test was in agreement with the low hardness of the Ti. Mechanical properties of the film were found to be uniform and the AFM picture (Fig. 8) showed the surface being smooth, however, decorated with separate particles grown on it.

Fig. 5 Hardness of the sample G54 investigated surface 8x8 mm2
Conclusion

The films formed up to 200 min, when deposited from RMDSNH₃N₂ mixtures, generally contained a lower oxygen, carbon, and nitrogen. Two reasons for the oxygen present could be taken into account. 1. Pollution of the gas mixture introduced to the reactor. 2. Effects of atmospheric oxygen on the film components when taken out of the reactor. Organic species (CH groups) were found in the films deposited at lower 1 N₂H₄ and 200 C, and with low ammonia concentration in the gas mixture RMDSNH₃N₂ at 1 N₂H₄. On the other hand, at 1 N₂H₄ and RMDSNH₃N₂ = 1, the carbon content was smaller than in most cases recorded. The N₂H₄, and the absorption bands of CH groups were detectable in infrared spectra for all of the range 1 N₂H₄ and hollow growth of NH₃. No significant nitrogen content in the deposit was found by XPS measurement. For those films, when considering the overall formula SiON:C, the relationship has been estimated.

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References