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STUDY OF THE CHARACTERISTICS OF INORGANIC LAYERS OBTAINED BY PLASMA-CHEMICAL PRECIPITATION ON POLYMERS

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Résumé - Les méthodes de l'XPS, la spectroscopie IR de la réflexion de surface et la spectroscopie électronique ont été utilisées pour l'étude des couches inorganiques obtenues sur le polymère pendant la synthèse plasmochimique. Les couches de Si_3N_4 , AlN , SiO_2 ont été synthétisées sur la surface des polyimides par des méthodes plasmochimiques diverses. Les investigations par la méthode XPS ont démontrées que le substrat polymérique participe activement au processus de la synthèse. L'étude par la microscopie électronique des étapes initiales a démontrée que la croissance commence par la formation de noyaux ayant la structure de dendrites typiques pour les couches polymériques déposées. Les résultats expérimentaux permettent de tirer la conclusion qu'il est possible d'obtenir les diverses structures polymère-inorganiques à l'exception entièrement de l'interface.

Abstract - Inorganic films obtained on the polymer support during plasma-chemical synthesis have investigated by XPS, IR-reflectance spectroscopy and SEM. The layers of Si_3N_4 , AlN , SiO_2 were obtained of plasma chemical precipitation on the surface of polyimide films. The results of XPS investigations showed that the polymer support takes an active part in the formation of the inorganic film. The data of electron microscopy in the initial stages of film growth indicate that in the first stage nuclei are formed. They are uniformly distributed on the surface of the polymer support and exhibit a pronounced dendrite structure. The experimental results suggest that under experimental conditions makes it possible to obtain various polymer-inorganic structure devoid of the interface.

INTRODUCTION

At present the plasma-chemical treatment of various materials including polymers is one of the most rapidly developing trends in material science. The plasma-chemical precipitation of various inorganic layers (Si_3N_4 , AlN , SiO_2 , etc.) on neutral supports (semiconductors and metals) has long ago become one of the most important technological operations in the microelectronic production /1,2/. The properties of these layers have been studied by different methods and the main efforts of the researchers is directed to the establishment of the correlation between the conditions of precipitation and synthesis and the characteristics of the layers.

The treatment of the polymers in plasma for imparting new properties to the surface by depositing on it quasi-polymer layers one also known and widely investigated and used /3/. When the synthesis of polymer layers is carried out under the conditions of non-equilibrium low-temperature plasma, a

plasma-forming gas, organic monomers and fragments of macromolecules are used. As a result of the synthesis, a layer is formed the stoichiometry of which is close to that of the polymer. In structure it is usually a densely cross-linked system. These layers may be deposited on any organic and inorganic substrates.

In our opinion, the plasma-chemical treatment of organic and inorganic materials has many similar features: virtually the same technological equipment and certain similarity between the chemical and physical processes of layer formation. However, there are differences between the plasma-chemical synthesis of quasi-polymer layers on the polymer surface and the deposition of inorganic layers on the surface of the semiconductor. This is mainly due to the role played by the substrate. Inorganic substrate is neutral component, whereas a polymer substrate can probably take part in the process.

Hence, it is interesting to obtain an inorganic layer on the polymer surface by plasma-chemical deposition and to investigate its characteristics. This is the purpose of the present paper.

EXPERIMENTAL METHODS

The SiO_2 , Si_3N_4 and AlN films were obtained by the plasma-chemical growth on a polymer. The properties of silicon nitride layers grown on polyimide were investigated.

Silicon nitride films deposited on polyimide in a specially constructed experimental installation ensuring the possibility of placing it outside the initiation range of high frequency discharge (Fig.1). $\text{SiH}_4 + 4\% \text{ Ar}$ and N_2 (high purity) were used as initial substances. N_2 was introduced into one of the reactor chambers in which the low-temperature glow-discharge plasma was generated. The high frequency discharge plasma was excited in accordance with the inductive scheme at a frequency of 1.76 MHz and a generator power of 2 KW. The nitrogen plasma was directed into the second reactor chamber into which an argon-silane mixture was also charged where the substrate was placed on a heater. The silicon nitride films were deposited on substrate heated to 600 K at the overall pressure of the reaction mixture in the reactor 50-60 Pa. Polyimide of the following chemical formula was used as the substrate:

(Kapton-H)

the film thickness was 40 μm . This polymer was chosen because it is a high-temperature dielectric stable to ionizing radiation [4]. Polyimide was coated with silicon nitride of different thicknesses (from 50 to 1500 Å). The thickness was checked by simultaneous deposition of silicon nitride on a silicon substrate. The layers were investigated by different methods.

The XPS-spectra were taken on an Kratos XSAM-800 spectrometers with the excitation by X-ray Mg-radiation with an energy of 1253.7 eV. Binding ener-

Figure 1. Schematic diagram of plasma-chemical installation

gies have been determined by using the C 1s peak (from in situ contamination) at 285 eV. The survey spectra at a binding energy of 0-1000 eV and spectra of single-photoelectron lines C 1s, N 1s, O 1s and Si 2p were taken. The recording of spectra and the mathematical processing were carried out with DS-800 system. The precision of the binding energy determination was 0.1 eV and that of the quantitative analysis was 10%. The IR-reflection spectra were recorded with a Perkin Elmer 580 B spectrophotometer. The topology of the layers was studied with a Hitachi-750 scanning electron microscope.

RESULTS

Survey spectra of the silicon nitride layers of different thicknesses on a Kapton-H polymer film showed that with increasing layer thickness the intensity of Si 2p and N 1s peaks increases and that of C 1s peaks decreases. The analysis of the fine structure shows that the peaks are superpositions of several peaks. This may be related to the fact that different types of covalent bonds are present in the layers obtained by this method. Fig.2 and 3 show the fine structure of the Si 2p peaks for layers of different thicknesses.

The mathematical processing of XPS high-resolution spectra made it possible to determine the binding energy and atomic concentration for each element. These values are given in Table 1. The table shows that when the layer thickness increases, the atomic concentration of element changes and shifts in binding energy appear. These shifts are usually caused by the excess negative charge generated by the surrounding sphere consisting of the charges of neighbouring ions located at different distances from the central ion [5]. In our case this shift indicates that the number of ions in the coordination sphere changes. The XPS spectra of a model compound, silicon oxynitride (ICS, USSR), were also analysed. The results are given in Table 2.

The analysis of reflection spectra obtained from the same surface mode it

Figure 2. Si 2p XPS spectra for a silicon nitride layer 100 Å thick; curve resolved to show two peaks

Figure 3. Si 2p XPS spectra for a silicon nitride layer 1000 Å thick; curve resolved to show two peaks.

TABLE 1. Binding Energies (BE) and Atomic Concentration (AC) for Si, N, O and C on the surface of polyimide films.

Thickness of deposition layer, Å	Si 2p		N 1s		O 1s		C 1s	
	BE, eV	AC, %	BE, eV	AC, %	BE, eV	AC, %	BE, eV	AC, %
1. 100	102.3	14.26	398.2	11.5	532.5	19.76	285.0	14.41
	103.5	11.80	399.3	4.69	533.5	13.46	286.2	4.90
			400.6	0.96			288.3	2.35
2. 1000	102.1	16.08	398.2	20.32	532.4	7.97	285.0	18.14
	103.3	14.22			533.1	19.07		

possible to identify some characteristic bands. The presence of an absorban-

ce band with a maximum of $840\text{--}850\text{ cm}^{-1}$ indicates S-N stretching vibrations in silicon nitride. The presence of hydrogen bonded in the form of Si-H group in films $1000\text{ \AA}$ - thick was observed at 2170 cm^{-1} . The $1020\text{--}1060\text{ cm}^{-1}$ bands may assigned to Si-O-Si and Si-O-C chemical bonds. A wide band at the range of 3600 cm^{-1} may be assigned to the stretching vibration of the free Si-OH group. The analysis of the results of investigation of film surfaces with layers less than $100\text{ \AA}$ in thickness is some what difficult because characteristics polyimide bands are present in the ranges of $800\text{--}900\text{ cm}^{-1}$, 1020 cm^{-1} , etc. However, it is possible to single out the characteristic bands of the bonds formed after treatment, such as C=O stretching vibrations of 1655 cm^{-1} in the NH-C=O. The 1620 cm^{-1} band is assigned to bending vibrations of amide-II. This is in good agreement with the XPS data and indicate that the polymer substrate is destroyed during the synthesis.

TABLE II. Binding Energies for Silicon Oxynitride

	Si 2p	N 1s	O 1s
BE, eV	102.3	398.2	533.0
	104.0		

The initial stages of film growth and the topology of continuous layer, is naturally, of the greatest interest. Fig. 4 shows the micrographs of a surface with a growing inorganic layer. Fig. 4a shows a high concentration of nuclei of different types. Fig. 4b and C show the fine structure of a typical nuclei-es. The nuclei are usually of the dendrite type. It is noteworthy that the number of nuclei is high and their sizes are quite different. Fig. 5 shows the surface of a silicon nitride layer $1000\text{ \AA}$ -thick. It is clear that after the nuclei coalesce, usual regular film growth takes place. Moreover, the comparison of Fig. 4c and 5 shows, that the relief of this layer virtually does not differ from that of the initial polymer film. Pores and other similar defects were not detected.

DISCUSSION

The comparison of the results given in Table 1 and shown in electron micrographs of the layers shows that the surface of sample 1 is an island structure of the new phase on the surface of the polyimide film. The surface of sample 2 is a continuous layer formed as a result of the plasma-chemical synthesis. The depth of the XPS analysis is $50\text{--}70\text{ \AA}$, hence, in case 1 both the new phase and the surface of the polyimide film after treatment in plasma were analyzed. In the second case only the new synthesizes layer was analyzed. It can be seen from Table 1 that the surface of sample 1 is a more complex structure than that of sample 2.

Now the results of XPS of the surface layer of sample 2 will be considered. Si 2p - 102.3 eV binding energy can be assigned to the S-N chemical bond whereas 103.3 eV can be assigned to the S-O bond /6/. The position of the N

Figure 4. Scanning electron microscope picture from a surface covered with silicon nitride layer. 100 Å-thick. (a) Magnification x500. (b) Magnification x2000.

Figure 4(c). Magnification x10000.

1s peak is higher than that of the individual compound, 397.5 eV, which is probably due to the presence of a more electronegative O atom in the environment. The O 1s, 532.5 eV, line, in turn, also indicates that silicon oxide (533.0 eV BE) can be formed. As already the shift in BE is determined by the excess negative charges of the coordination sphere. Hence, compounds of the following types: Si-N-O, O-Si-N, C-Si-O, etc., can exist in the island struc-

Figure 5. Scanning electron microscope picture from a surface covered with silicon nitride layer 1000 Å-thick. Magnification x10000.

ture on the polymer surface.

Table 2 shows that the data obtained from XPS-spectra of the model compound agree with those obtained for the surface layers, and it can be stated that silicon oxynitride is present in a surface layer of samples. The presence of the O 1s 532.4 eV and 533.1 eV BE indicates that both silicon oxynitride and silicon oxide can be formed. The C 1s 285.0 eV peak may be either a signal of hydrocarbons located on the film surface transported there from the vacuum system of the spectrometers (sample 2) or a signal typical of the benzene ring (sample 1). The 286.6 eV BE may be assigned to oxygen-containing functional groups, such as C-O, C-OOH and C-O-C=O /7/, whereas the 288.3 eV BE can be assigned to amide and imide groups. The position of the N 1s 399.3 eV and 400.6 eV BE may be assigned to nitrogen-containing amide and imide groups /8/. It should be noted that the atomic concentration of elements being the products of polyimide degradation is much lower than that of the products of inorganic synthesis and evidently decreases with the increasing thickness of the layer as shown by sample 2.

There is an interesting in the treatment of the chemical structure of inorganic layers. This fact is probably due to high oxygen concentration in the surface layer. This high concentration cannot be ensured by the products of polymer degradation alone the condition of plasma-chemical synthesis cannot be the reason for this high concentration either. Most probably, this high oxygen concentration on the surface is caused by the interaction between the surface (activated as a result of the interaction with the plasma) and the atmosphere. Hence, the surface becomes covered by "quasisiliconoxide". The total stoichiometric composition of the surface (assuming that the 285.0 eV BE in both cases refers to hydrocarbons) is $\text{Si}_{1.00}\text{O}_{1.37}\text{N}_{0.65}\text{C}_{0.28}$ for film 1

and $\text{Si}_{1.00}\text{O}_{0.73}\text{N}_{0.66}$ for film 2.

In this work we did not intend to analyze in detail the mechanisms of generation, growth and coalescence of nuclei. However, the quantity and the variations of types and sizes observed in the photos (Fig.4 and 5) suggest that the nuclei with the critical radius can be very small under the experimental conditions (a few atoms or even smaller). This fact, in turn, shows that chemical interactions take place between the plasma elements and the surface, and the polymer participates very actively in the formation of the layer. In this situation the growth of the nucleies proceeds most probably as a result of the attachment of particles from the gas phase because the diffusion of these very active particles by any considerable distance along the surface is improbable.

The dendrite structure of the nuclei (Fig.4B) shows, in our opinion, that, at least in the initial period the fragments of the polymer molecules actively participate in nucleation and the nuclei have a complex polymer-inorganic composition. This is even more probable because the dendrite structure is usually observed in the deposition of a thermally evaporated polymer on various substrates /9/. There is probably a certain similarity between the process of the thermal deposition of the polymer on a substrate and the process described here. In the latter case the polymer substrate takes the most active part in layer formation.

The above data make it possible to develop in the most approximate form a model for formation of the inorganic layer on the polymer surface. The polymer heated to T 573 K is placed outside the active zone but is nevertheless submitted to a continuous action of the plasma components. At high temperature this action may lead to catostrophic changes in the polymer surface. The chemical bonds on the surface break, and radical are generated at high concentration. At this conditions the polymer surface may be a "continuous free radical". In the region near the surface, a considerable concentration of gaseous degradation products of the polymer (the fragments of the main structure) is observed. The plasma elements in this region react with degradation products and then touching the surface form covalent bonds with it. Consequently, the primary structure of layers obtained by plasma-chemical deposition is a complex polymer-inorganic composite consisting of the elements of the active gas and the polymer degradation products covalently bonded to each other and to the polymer surface.

Table 1 (sample 1) and Fig.4 provide direct confirmations of this process. As the process continues and the area of the new phase increases. As a result, the concentration of degradation products in the layer near the surface decreases. As the distance between the film surface and the tentative boundary between the polymer and the inorganic layer increases, the structure of the layer becomes determined to the increasing extent by the conditions of

of the synthesis.

Hence, when the inorganic layer is deposited on a polymer film, a fundamentally new structure: a polymer-inorganic intermediate layer which forms a part of both the polymer and the inorganic layer to the some extent and makes it possible to obtain various polymer-inorganic structure devoid of the interface.

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