The electrochemical deposition of silicon - carbon thin films from organic solution

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Abstract. Silicon - carbon thin films were obtained on silicon substrate by using electrochemical deposition at room temperature and atmospheric pressure. Solution of electrochemical deposition was consisted of methanol or ethanol and hexamethyldisilazane ((CH₃)₃-Si-NH-Si-(CH₃)₃, HMDSN). It was shown that a type of electrolyte is strongly effect on maximum current density and the morphology of the deposited film.

1. Introduction
The synthesis of silicon-carbon films has been widely studied due to their attractive properties, such as wear resistance, chemically inertness, and wide band gap, which have already provided optical, electronic and other applications in aggressive ambient. Silicon - carbon films are very interesting and important material for microelectronics. These films are used for gas sensors, ultracapacitors, field emission devices and other applications in aggressive ambient [1]. There are many methods for obtaining these films, such as magnetron sputtering [2], ion sputtering, chemical vapor deposition, pulsed laser deposition, electrochemical deposition from molten salt, sol – gel method [3-5]. The applications of these methods, however, have been limited, owing to the complex equipment and rigorous experimental conditions, including high vacuum and high temperature.

There is experimental evidence that most materials which can be deposited from the vapor phase can also be deposited in liquid phase using electroplating techniques and vice versa [6]. Enlightened by this conclusion, Namba [7] first attempted to grow diamond phase carbon films in the ethanol solution at a temperature less than 70 °C. From the application viewpoint, the liquid deposition techniques have many advantages such as availability for large area deposition on intricate surfaces, low deposition temperature, low consumption of energy, and simplicity of the set up, over the vapor deposition techniques.

The possibility of deposition of diamond-like carbon films by means of electrolysis of organic liquids such as methanol [8], acetonitrile [9], dimethylsulfoxide [10], and lithium acetylide in dimethylsulfoxide [11, 12], at atmospheric pressure and low temperature, has been demonstrated recently.

However, not much has been reported on the profound of electrochemical deposition of silicon-carbon films from a methanol or ethanol solution of hexamethyldisilazane. So, only Yan [13] performed a successful electrochemical deposition of silicon carbide nitride nanocomposite films from methanol solution of hexamethyldisilazane that led to the formation of the Si₃N₄ and SiC crystalline grains.
In this work, an electrochemical route to deposit silicon-carbon films from a methanol and ethanol solution of HMDSN at atmospheric pressure and low temperature has been reported. Methanol was also selected because its polarizability and conductivity are stronger than those of ethanol.

2. Experimental

The electrolytic deposition system was used to obtain silicon-carbon films. A schematic diagram of the system is shown in Figure 1.

![Figure 1](image-url)

**Figure 1.** Schematic structure of electrolytic deposition system (1 - glass cell, 2 - dielectric cover, 3 - graphite anode, 4 - cathode - substrate, 5 - solution, 6 - thermocouple, 7 - clamps, 8 - thermal table, 9 - voltmeter of thermocouple, 10 - ammeter, 11 - HV-voltmeter, 12 - power supply).

Silicon-carbon film was deposited on silicon substrate (100), with a size of 12x17x0.4 mm³ and resistivity of 4.5 Ohm·cm. First, the substrate was dipped in the HF solution for a few minutes. Silicon substrate was mounted on the negative electrode and graphite was mounted on the positive electrode. The distance between the substrate and positive electrode was set to 10 mm. The deposition was done from two types of solution: 1 - a methanol solution of HMDSN; 2 - an ethanol solution of HMDSN. HMDSN was dissolved in analytically pure methanol (ethanol), with the volume ratio of HMDSN to methanol (ethanol) to be 1:9. The cleaned substrate was placed into the above solution, with an area of 10·15 mm² to be immerged therein. The films were deposited for 4 h at 60°C. The applied potential was 270 and 450 V, for methanol and ethanol solutions respectively.

Figure 2 shows the curves of current dependence on the deposition time for two types of solution. During the deposition for the nanocomposite film, we found that the current density decreased from 70 mA/cm² to less than 35 mA/cm² with increasing the deposition time for a methanol solution of HMDSN and from 42 mA/cm² to 15 mA/cm² for an ethanol solution of HMDSN. In both cases, a gray film was obtained on the cathode Si substrate after deposition. The thickness was measured to be about 800-900 nm using interferometer technique. It means the average deposition rate is ~212 nm/h.
Figure 2. Current dependence on time deposition (1 - methanol - HMDSN solution; 2 - ethanol - HMDSN solution).

Most part of the current decreased within the first hour for methanol – HMDSN solution while significant current decrease ethanol – HMDSN solution is observed during the first two hours. This fact may be explained by a decrease of reaction products, increase of film thickness and different deposition rate for two types of solutions.

Namba [7] thought that the substrate current played an important role in film formation from an organic solution. The conductivity of electrolyte is indeed an important factor during electrolysis. Namba used ethanol as electrolyte, and the maximum current density was only 5 mA/cm², whereas in our experiment, the current density exceeded 42 mA/cm². Yan [13] used methanol as electrolyte, and the maximum current density was about 40 mA/cm², whereas in our case the current density exceeded 70 mA/cm². So, we see that methanol electrolyte is more promising for silicon-carbon films deposition. Methanol has active CH₃ species which concentrate near the negative electrode surface and prefer the formation of diamond-like carbon film by electrochemical reactions.

The molecule of HMDSN also contains electron-donating methyl group, which displays somewhat positive charge due to their low electro-negativity. Consequently, the molecules are liable to be absorbed on the surface of the negative electrode owing to the sorption of the electrons on the cathode surface. So the Si–C and Si–N bonds in HMDSN molecule will be dissociated to form some silicon-containing clusters like (SiC)x and (SiN)x. The clusters are deposited on the cathode substrate, and form b-Si₃N₄, a-Si₃N₄, and SiC nanoparticles finally [13].

Figure 3 shows SEM micrographs of the deposited films which were taken by SEM Zeiss Merlin compact VP-60-13. From the Fig.3a it can be seen that film deposited from ethanol solution is composed of small, compact grains. The average grain size is about 130 nm. The morphology of the film deposited from methanol solution is rather different and characterize with a rougher surface emerges with nodular-like features (Fig.3 b).
3. Conclusions

Silicon-carbon films can be obtained from methanol-HMDSN and ethanol-HMDSN solutions by the electrochemical deposition. This simple method may extend the field of application silicon-carbon films in future. This synthesis strategy may be transferred to fabricating other inorganic nanocomposite films, using appropriate organic reagent and electrolysis condition.

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