DC GLOW DISCHARGE FOR SYNTHESIS DIAMOND FILMS WITH HIGH GROWTH RATE

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The results of experiments on further investigation of the growth kinetics of diamond films in a dc glow discharge on modernized equipment are presented. As a result of the research, it was possible to expand the possibilities of using equipment for the synthesis of diamond films in a glow discharge with a grounded substrate holder. The diamond film growth rates were 3-4 times higher than those obtained in earlier experiments while maintaining high structural characteristics of the synthesized diamond film. The maximum growth rate was 12 μm/h at the pressure of the hydrogen-methane mixture in the discharge chamber of 180 mm Hg. The possibility of obtaining both polycrystalline diamond films without pronounced texture and high-textured diamond films with an orientation of the surface of diamond crystallites (100) parallel to the sample surface is demonstrated. Thus, the presented hydrogen-methane mixture activation system for the synthesis of diamond films is promising for use in technological applications.

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INTRODUCTION

Most of the experimental and technological set-ups existing in the world use the microwave method of activation of the hydrogen-methane gas mixture for the synthesis of diamond films. At the same time, intensive research is underway on the use of other activation methods. One of such methods of activation of a gas mixture is a glow discharge in its various modifications [1-3]. Such studies are conducted with the aim of reducing the cost of existing experimental equipment and increasing the efficiency of diamond synthesis processes, i.e. reduction of the invested energy consumption per carat of the obtained diamond. The investigations were carried out with cathodes from various materials (tungsten, molybdenum, tantalum) and at various temperatures of the cathode, i.e. with a cold and hot cathode [2, 4]. In general, when using a glow discharge as a tool for the synthesis of diamond films, some progress has been made in the world [5].

Studies on the use of glow discharge for the synthesis of polycrystalline diamond coatings have been conducted in the NSC KIPT for a number of years. Positive results were obtained using a glow discharge stabilized by a magnetic field; while the substrate holder was under the floating potential [6]. Later, the laboratory equipment was upgraded to avoid ion bombardment of substrate during the synthesis of diamond films. A flat cylindrical cathode was used and the anode was a substrate holder [7]. As it was shown earlier, it was possible to achieve stable parameters of diamond films synthesis at a pressure of 100 mm Hg. The growth rate did not exceed 3 μm/h, which is clearly not enough for the deposition of films with a thickness of more than 100 μm [8]. Thus, the purpose of the work was to expand the capabilities of modernized equipment, to determine the conditions for stable burning of a glow discharge at pressures above 100 mm Hg and to obtain high-quality diamond films with a higher growth rate.

EXPERIMENTAL

The experiments were carried out with a cathode of 66 mm in diameter, and the substrate holder, which served as an anode and had a diameter of 42 mm. The stability of the discharge combustion in this system depends on the geometric parameters of the discharge system (the ratio of the distance between the cathode and the anode to the diameter of the anode). If this ratio is not optimally at a certain pressure, the discharge passes from the normal glow discharge to the anomalous one with further disruption to the arc. The temperature of the substrate holder falls sharply (Fig. 1,a), while the power input into the discharge continues to increase linearly (see Fig. 1,b).

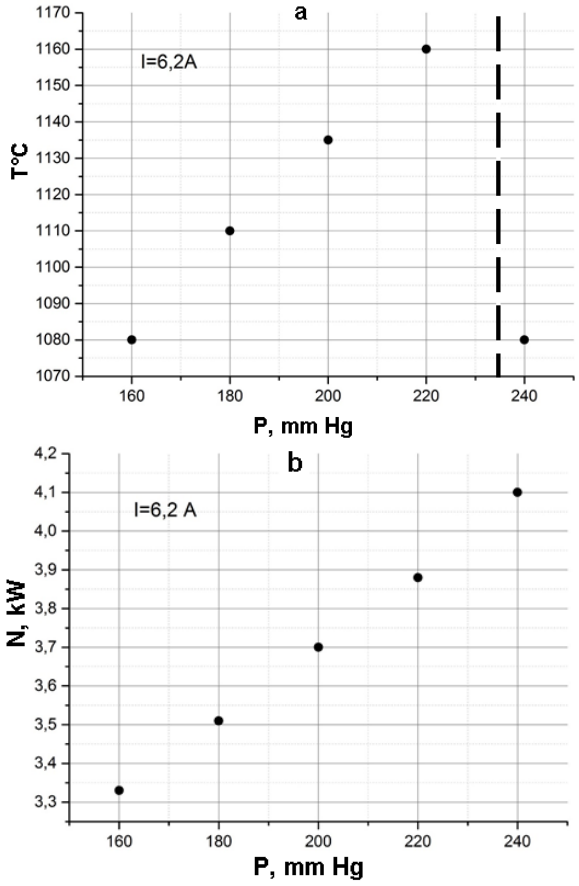

Fig. 1. Dependences: a – substrate temperature vs pressure; b – inputted power into the discharge vs the pressure

As a result of variations of the geometric parameters in the discharge system, it was possible to achieve stable burning of the discharge in hydrogen medium up to a pressure of 240 mm Hg (Fig. 2).

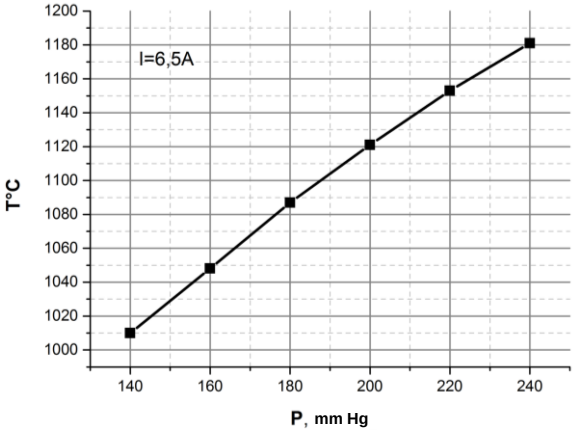

Fig. 2. Dependence of the substrate temperature vs the hydrogen pressure in the discharge chamber

The discharge remained as the normal glow discharge, i.e. with increasing discharge current the voltage between the cathode and the anode did not increase; the temperature of the substrate holder increased proportionately in this case. The obtained results made it possible to carry out a number of experiments on the synthesis of diamond films in the pressure range from 110 to 180 mm Hg. Synthesis of diamond films was carried out in a hydrogen-methane mixture with a methane concentration in the discharge chamber from 1 to 6 %. The working gas flow varied from 75 to 335 cm^3/min. As substrates we used samples of single crystal silicon with dimensions of 8x8 mm and a thickness of 340 μm. For the formation of diamond film, the samples were previously seeded with a diamond powder with a grain size of 2…3 μm.

EXPERIMENTAL RESULTS

It is known that the deposition rate of a diamond film depends on the ratio of the concentration of hydrocarbon radicals responsible for diamond growth and the concentration of atomic hydrogen. Therefore, as the pressure of the gas medium increases, it is necessary to increase the concentration of methane in the mixture in order to ensure the maximum growth rate. The conducted studies have shown that for the maximum growth rate of a diamond film at pressures of 100…110 mm Hg. 1 % of methane is sufficient, whereas at a pressure of 180 mm Hg the optimum concentration of methane in hydrogen was already from 3 to 4 %. The growth rate varied from 3.5 μm/h at 1…1.5 % methane and pressure of 110 mm Hg up to 7.5…8 μm/h, with a methane concentration of 2.5 % and a pressure of 160 mm Hg. The best results were obtained with a gas pressure in the discharge chamber of 180 mm Hg and methane concentrations in the range from 3 to 4 %. The growth rate of the diamond film reached 12 μm/h (Fig. 3).

The growth rate was determined by a weighting method with averaging over 9 samples of single-crystal silicon, 340 μm in thickness and 8×8 mm in size. With an increase in the concentration of methane in hydrogen above 4 %, i.e. up to 5…6 %, the growth rate decreased monotonically up to 9...10 μm/h (see black point in Fig. 3). This is due to the fact, that with increasing methane concentration in the discharge above a certain limit, there is already not enough atomic hydrogen to completely remove the non-diamond carbon impurity depositing on the surface of the growing diamond film. We note that the power input into the discharge did not exceed 4.5 kW at a discharge current from 5 to 7 A, which is much less than in previously published papers [9].

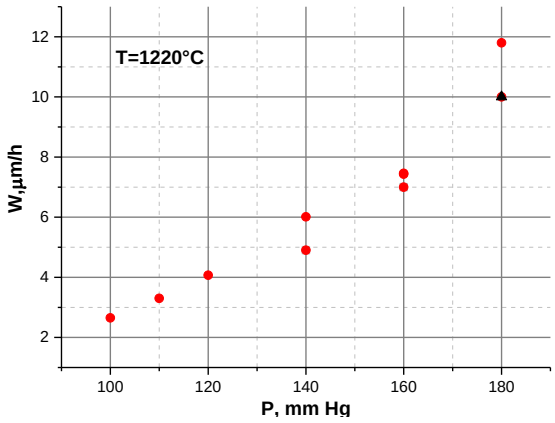

Fig. 3. Dependence of the growth rate of a diamond film vs the pressure of the hydrogen-methane mixture in the discharge chamber

As a result of the experiments, diamond films with thicknesses from 20 to 250 μm were obtained on silicon substrates. A general view of a polycrystalline diamond film with a thickness of 210 μm, without pronounced texturing of the surface, is shown in Fig. 4. It should be specially noted that when the diamond films thicknesses exceeding 100 μm there were not observed cracks on the growing diamond surface, and there was not the diamond film peeling from the silicon substrate. Such effects were quite often observed in earlier experiments using a glow discharge stabilized by a magnetic field, where the substrate holder was under a floating potential, and the anode was a ring insert [10].

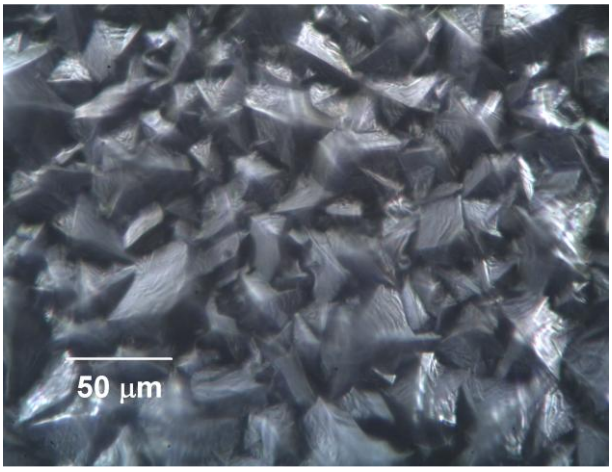

Fig. 4. View of polycrystalline diamond film with a thickness of 210 μm. The crystallite size is 40…50 μm

The floating potential on the substrate holder was 200 V or more, which led to ion bombardment of the

growing surface. This process could cause the formation of defects, which led to stresses between the diamond film and the silicon substrate. Especially these negative processes affected the growth of high-quality diamond films ($\rho \geq 10^{14}$ Ω·cm), because the intergrain distances sharply decreased, which served as "unloading" of the stresses arising during the growth process. In the current experiments the substrate holder was under zero potential, i.e. itself served as an anode, which precluded the bombardment of it by ions.

While maintaining certain synthesis parameters such as temperature, methane concentration in hydrogen medium, gas mixture pressure, it was possible to obtain well-textured diamond films with the orientation of diamond crystallites (100) parallel to the sample surface. Diamond films with this orientation up to 100 μm were obtained. Fig. 5 shows the view of textured diamond film at the initial stage of growth. The film thickness is of 20 μm, the crystallite size is of 4…5 μm.

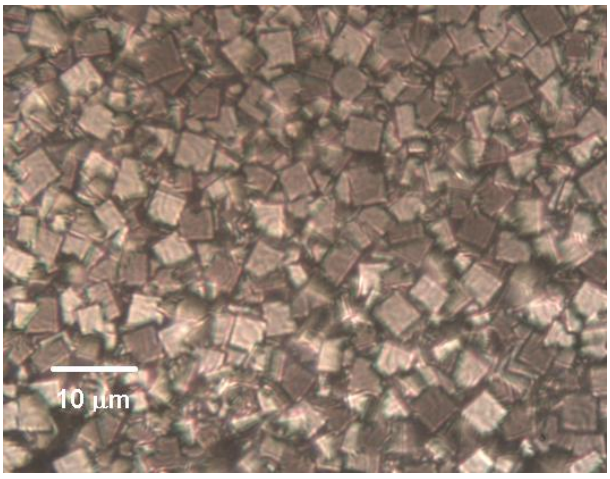

Fig. 5. View of diamond film with texture (100) the thickness is of 20 μm, the crystallite size is of 4…5 μm

However, a more complete understanding of the growth processes of textured diamond films requires further research.

CONCLUSIONS

1. As a result of the research, it was possible to expand the possibilities of using equipment for the synthesis of diamond films in a glow discharge with a grounded substrate holder.

2. The diamond film growth rates were 3…4 times higher than those obtained in earlier experiments while maintaining high structural characteristics of the synthesized diamond film.

3. The possibility of obtaining both polycrystalline diamond films without pronounced texture and high-textured diamond films with an orientation of the surface of diamond crystallites (100) parallel to the sample surface is demonstrated.

4. The presented system of activation of hydrogen-methane mixture for the synthesis of diamond coatings is promising for use in technological purposes.

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ТЛЕЮЩИЙ РАЗРЯД ПОСТОЯННОГО ТОКА ДЛЯ СИНТЕЗА АЛМАЗНЫХ ПЛЕНОК С ВЫСОКОЙ СКОРОСТЬЮ РОСТА

В.И. Грицына, О.А. Опалев, В.Е. Стрельницкий

Приведены результаты экспериментов по дальнейшему исследованию кинетики роста алмазных пленок в тлеющем разряде постоянного тока на модернизированном оборудовании. В результате проведенных исследований удалось расширить возможности применения оборудования для синтеза алмазных пленок в тлеющем разряде с заземленным подложкодержателем. Были достигнуты скорости роста алмазной пленки, в 3-4 раза превышающие полученные в более ранних экспериментах при сохранении высоких структурных характеристик синтезируемой алмазной пленки. Полученная максимальная скорость роста составила 12 мкм/ч при давлении водородно-метановой смеси в камере разряда 180 мм рт. ст. Показана возможность получения как поликристаллических алмазных пленок без явно выраженной текстуры, так и высокотекстурированных алмазных пленок с ориентацией поверхности кристаллитов алмаза (100) параллельно поверхности образца. Таким образом, представленная система активации водородно-метановой смеси для синтеза алмазного материала представляется перспективной для применения в технологических целях.

ТЛІЮЧИЙ РОЗРЯД ПОСТІЙНОГО СТРУМУ ДЛЯ СИНТЕЗУ АЛМАЗНИХ ПЛІВОК З ВИСОКОЇ ШВИДКІСТЮ РОСТУ

В.І. Грицина, О.А. Опалєв, В.Є. Стрельницький

Наведено результати експериментів щодо подальшого дослідження кінетики росту алмазних плівок у тліючому розряді постійного струму на модернізованому обладнанні. В результаті проведених досліджень вдалося розширити можливості застосування обладнання для синтезу алмазних плівок у тліючому розряді з заземленим підкладкотримачем. Були досягнуті швидкості росту алмазної плівки, що в 3-4 рази перевищують отримані в попередніх експериментах при збереженні високих структурних характеристик синтезованої алмазної плівки. Отримана максимальна швидкість росту склала 12 мкм/год при тиску воднево-метанової суміші в камері розряду 180 мм рт. ст. Показана можливість отримання як полікристалічних алмазних плівок без явно вираженої текстури, так і високотекстурірованих алмазних плівок з орієнтацією поверхні кристалітів алмазу (100) паралельно поверхні зразка. Таким чином, представлена система активації воднево-метанової суміші для синтезу алмазних плівок представляється перспективною для застосування в технологічних цілях.