

Theoretical Evaluation of Possibility to Control Nucleation and Growth of Heteroepitaxial Carbon Films by Applied Fields

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Abstract

On the basis of the literature review, comparison of physical and chemical properties of materials and calculations, it was showed that the copper, saturated with hydrogen, is an appropriate substrate material for heteroepitaxial growth of diamond films. The atomic hydrogen in tetrapores of copper crystalline lattice will be the crystallisation centre of carbon. Herewith the difference in lattice cell parameters between the substrate and the growing diamond film is considerably reduced, *i.e.* epitaxial growth of crystal is possible. Besides, the disposition of tetrapores on the copper surface (111) and, respectively, of atomic hydrogen located in them, creates conditions for preferential formation of tetragonal bonds of carbon.

The estimations have shown that it is possible to create conditions for preferential oriented growth of diamond films through changing the magnitude and configuration of applied fields.

Introduction

The significant efforts devoted to synthesis of diamonds were motivated by the unique combination of properties of this material. They give chance to produce electronic devices, both in discrete and integrate forms, with the highest speed and power, with a huge working temperature range, with a high element density, and with increased mechanical strength and reliability.

Various techniques, plasma-enhanced chemical vapour deposition (CVD), ion-assisted deposition, and hot filament CVD in obtaining diamond films have been developed and today are widely used [1-6]. However, the characteristics achieved thus far for electronic device are not good enough for practical applications.

The majority of the processes of CVD crystallisation occur in conditions of the massive chaotic crystallisation of diamonds those hinder obtaining of high quality crystals.

Therefore searching of systems, in which the rate of the backwards process would be noticeably high and, besides, would allow continuous control of film growth, is the most urgent problem, that solution will determine further development of diamond synthesis technology.

Problem statement and theoretical evaluation of applied field effects on the nucleation of heteroepitaxial carbon films

As is generally known, besides such specific problems as simultaneous nucleation of non-diamond structures, flawless hindering stable growth of the oriented diamond film, the problems related with controlled growth rates, selective elimination of highly defective areas and non-diamond structural modifications of carbon films are characteristic for processes of diamond synthesis.

The above-mentioned problems may be solved through technological control by applied fields (electrostatic, magnetic, optical, temperature, field of elastic deformations) of certain limiting symmetry group. Herewith the symmetry of fields should correspond to pointed and spaced symmetry group of the diamond and not correspond to the symmetry of non-diamond modifications of carbon films.

Evaluation of applied field effects on the nucleation

The nucleus formation and growth rate of a crystalline film are determined rather by difference of magnitudes of thermodynamic functions of vari-

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ous phase conditions, than by magnitudes themselves, the difference being substantially less compared with those magnitudes. Thus even the insignificant variations of thermodynamic functions in the applied fields effect on the process of nucleation and the rate and direction of the crystalline structure growth.

The energy of formation of nucleus (G_n) is determined by a chemical potential (μ) of a substance, by surface energy (σ) and, as a rule, by non-considered parameters, defining effects of applied fields and their space symmetry:

$$G_n = \mu + \sigma + W_C + W_E + W_H + W_{hv} + W_{SE} + W_{SH}$$

The additional members determine contributions of: W_E - energy of the electric field, W_H - energy of the magnetic field, W_C - energy of the field of elastic deformations, W_{hv} - energy of the optical influence, W_{SE} and W_{SH} - space symmetry of the applied fields (electric and magnetic fields).

Thus it is possible to create conditions for preferential nucleation and growth of a diamond film through changing the magnitude and the shape of applied fields.

Effects of elastic deformation field

The most convenient substrates for growing of diamond films would be the silicon monocrystalline plates, with a diamond-like structure, by virtue of their availability, cheapness and perspectives of further use in semiconductor instruments manufacture.

On the Fig. 1 a linear model of growth of a monolayer carbon film on the silicon is presented. Because of the difference of lattice cell parameters of Si (5.43 Å) and C (3.57 Å) [7] there are occurred elastic deformations of lattices. In the given model the deformation forces, effecting on the atom of carbon are equal to the double deformation forces effecting on the atom of silicon $F_C = 2F_{Si}$, so, the effects of all silicon substrate are substituted by effects of two silicon layers on one layer of carbon.

Let's write deformation force effecting on the atoms of carbon and silicon as:

$$F_C = C_C \frac{\epsilon_C}{a}, F_{Si} = C_{Si} \frac{\epsilon_{Si}}{b}$$

$$C_C \frac{\epsilon_C}{a} = 2C_{Si} \frac{\epsilon_{Si}}{b}$$

where C_C and C_{Si} - factors of an elasticity of carbon and silicon, ϵ_C and ϵ_{Si} - displacement, a and b - parameters of diamond and silicon lattices, respectively;

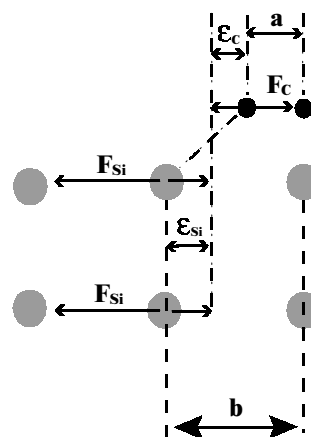


Fig.1. Linear model of monolayer carbon film growth on the silicon.

$$b - a = \epsilon_C + \epsilon_{Si}$$

Energy of elastic deformation of diamond lattice:

$$U_C = C_{11C} \left(\frac{\epsilon_C}{a} \right)^2 + C_{12C} \left(\frac{\epsilon_C}{a} \right)^2$$

$$U_C = 0.569 \times 10^{29}, \frac{\text{eV}}{\text{m}^3}$$

$$U_C = 0.322 \text{ eV, 1/atom}$$

Energy of elastic deformation of silicon lattice:

$$U_{Si} = C_{11Si} \left(\frac{\epsilon_{Si}}{b} \right)^2 + C_{12Si} \left(\frac{\epsilon_{Si}}{b} \right)^2$$

$$U_{Si} = 1.16 \times 10^{29}, \frac{\text{eV}}{\text{m}^3}$$

$$U_{Si} = 2.247 \text{ eV, 1/atom}$$

The estimated value of deformation energy of silicon and diamond lattices ($U_C + U_{Si}$) are equal: $(kT)/e = U_C + U_{Si} = 2.57 \text{ eV}$, what requires temperature about 30000 K to create such deformations. That evidences impossibility of epitaxial growth of high-crystalline diamond films on the silicon.

Thus, the buffer layer showing the following parameters is necessary to obtain high quality diamond films:

1. Diamond-like structure of a buffer layer;
2. Minimal difference between parameters of lattice cells;
3. Matching of the thermal expansion coefficient value to minimize thermal stresses between the substrate and the diamond films.

The analysis of physical and chemical properties of elements showed, that the copper, saturated with

hydrogen is by the acceptable material as a buffer layer for epitaxial growth of diamond films. On the Fig. 2 the copper surface (111) is given. The crystallographic calculations of tetrapore and octapore volumes in the copper lattice proved, that in copper film grown in a hydrogen medium the tetrapores will be filled-in with atomic hydrogen, and octapores with molecular hydrogen. The estimated value of space between the atomic hydrogen atom in tetrapore and carbon atom, deposited above tetrapore is $L=0.87 \text{ \AA}$, which is enough for C–H bond creation, because the length of C–H bond is 1.09 \AA [7].

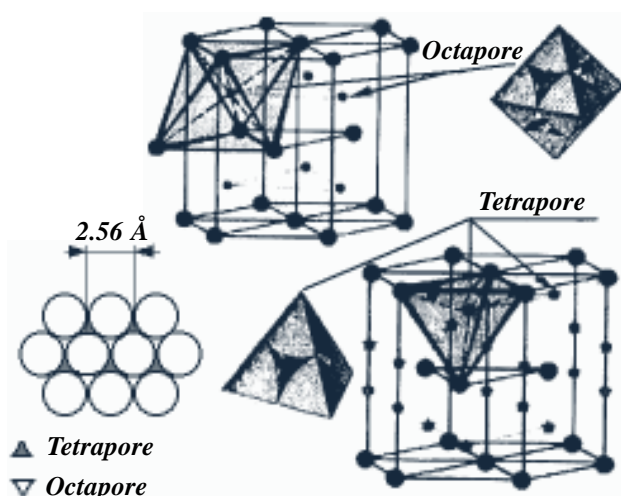


Fig. 2. Disposition of tetrapores and octapores on the surface of copper lattice (111).

Since copper does not create complex with carbon, the atomic hydrogen in tetrapores of the copper lattice will be centre of crystallisation of carbon, resulting in that the difference between lattice parameters for substrate and growing diamond film becomes considerably smaller.

Atomic carbon space on the surface (111) for diamond $a_D = 2.517 \text{ \AA}$ and for graphite $a_G = 2.84 \text{ \AA}$ [7].

Tetrapore space on the copper surface (111) $a_{Cu} = 2.56 \text{ \AA}$. *I.e.* the difference is:

$$\text{for diamond } \Delta_1 = \frac{2.56 - 2.517}{2.56} \times 100\% = 1.7\%$$

$$\text{for graphite } \Delta_2 = \left| \frac{2.56 - 2.84}{2.56} \right| \times 100\% = 10.94\%$$

Thus, the disposition of tetrapores on the copper surface (111) and respectively of atomic hydrogen located in them, create conditions for preferential formation of tetragonal carbon bonds.

Results of estimation of electrostatic field effects on energy conditions for diamond and graphite

The estimations of effects of the electrostatic field on the energy state of diamond and graphite nuclei, located in this field, were completed by limited version of the program ELCUT (<http://www.tor.ru/elcut>).

On the Fig. 3 the schematic model of the unit is presented.

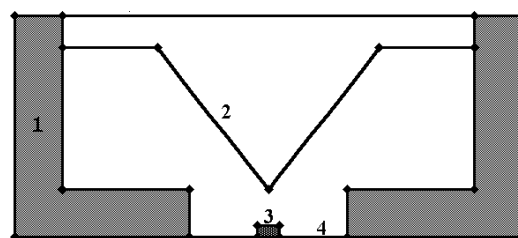


Fig. 3. Schematic model of the unit: 1 - quartz; 2 - anode; 3 - nuclei; 4 - substrate-cathode.

In the above-mentioned conditions of electrodes mounting the energy of electrostatic field is concentrated in the centre of substrate. Putting diamond and graphite nuclei of the various shapes in the centre of substrate the following results were obtained.

In the Fig. 4 the characteristic distribution of energy density of an electrostatic field is shown.

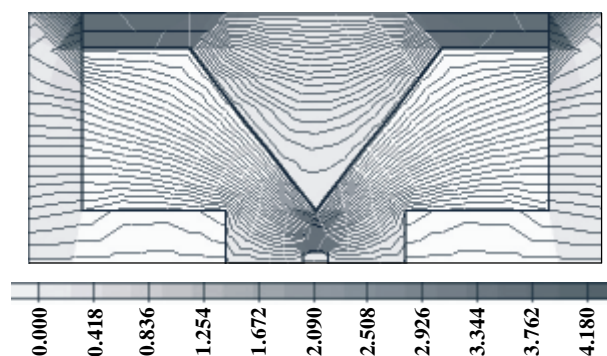




Fig. 4. Distribution of energy density of electrostatic field.

In the Table 1 density of electrostatic field energy in the bulk limited by nuclei of diamond and graphite and in the same bulk without nuclei in the vacuum is presented.

As it shown in Table 1 at the column growth the bulk energy increases in comparison with vacuum both for graphite and diamond. At growth along the sur-

Table 1

The density of electrostatic field energy in the bulk limited by nuclei of diamond and graphite, and in the same bulk without nuclei in the vacuum.

Material	Shape	The density of electrostatic field, $\times 10^{-10}$, J/m ³
Vacuum		2.667
Graphite		2.684
Diamond		5.807
Vacuum		2.504
Graphite		2.501
Diamond		1.288

face the energy density decreases in both cases, however, it decreases more for diamond nucleous. Thus, the growth along the substrate surface is the most favourable for diamond; and the columnar growth is unfavourable both for graphite and diamond.

Results of estimation of magnetic field effects on energy conditions for diamond and graphite

Similarly estimations for magnetic field were made. The calculations showed that constant magnetic field didn't influence considerably the energetically nuclei state due to tiny difference of magnetic susceptibilities for various carbon modifications (for diamond $\chi = -1.726 \times 10^{-12}$, for graphite $\chi_z = -51.665 \times 10^{-12}$, $\chi_x = -0.906 \times 10^{-12}$ [7]). However it influences on ions of carbon, deposited on the substrate. As shown in the work [8], the hardness of carbon films may be considerably increased if the magnetic field will be applied in process of film growing.

Not only intensity of the external fields influences the magnitudes of thermodynamic functions as well as coherence of fields' symmetry with the structure of crystalline film and its nuclei.

The copper structure saturated with hydrogen determines the symmetry of surface forces which is appropriate for a diamond structure.

Disposition of electrodes and their shapes should form the symmetry of cubic structure.

The static magnetic field creates the rotating mechanical moment in the structure of crystal and cir-

cular movements of atoms in the adsorption layer, which correspond to the presence of screw axes of the symmetry in diamond and to absence of those in the other modifications of carbon.

Conclusion

Thus, it was shown that the conditions for preferential nucleation and growth of a diamond film might be created through changing magnitude and shape of applied fields.

It was proved that to obtain high quality diamond films, the creation of a transitional buffer layer with diamond-like physical-chemical properties is necessary.

It was found that the copper, saturated with hydrogen, is an appropriate material for buffer layer with atomic hydrogen in tetrapores of the lattice, as a centre of crystallisation of a diamond film. The disposition of tetrapores on the copper surface (111) and, respectively, of atomic hydrogen located in them, create the conditions for preferential formation of tetragonal carbon bonds.

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