INVESTIGATION OF PLASMA COMPOSITION IN CVD DIAMOND DEPOSITION

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Introduction

The diamond is not only valuable as a gemstone, but its extreme properties relative to other materials make it an important and promising material for the industry. Due to scarcity and limited size of natural diamond these good properties cannot be used in lots of cases. Thus the synthesis of diamond has been researched for long time, in order to make possible such applications which cannot or very expensively could be exploited by bulk crystals.

The practical realization of diamond synthesis using chemical vapor deposition (CVD) has opened the way to several new applications, which are partly on the market already (e.g. cutting tools, coatings, optical windows).

Wide variety of substrates can be covered by polycrystalline diamond film using CVD method. Among substrates the silicon is the most common. The properties of polycrystalline layers in most of the cases are very similar to the single crystal layer. The good resistivity, high thermal conductivity and low dielectric constant together make diamond an excellent material for electronics. A new tendency in applications is the use of microcrystalline diamond in fusion reactors due to its good resistivity and high thermal conductivity. The fabrication of some MEMS and semiconductoctor device prefers the use of SOI (Silicon-on-insulator) wafers. Recently the SOD (silicon-on-diamond) wafers using diamond insulation layer instead of silicon dioxide are getting higher attention. The high power electronic applications requires single crystal layers, which currently can not be realized except on diamond and on very expensive boron-nitride substrates. Using homoepitaxial diamond functionality of several semiconductor devices with extreme properties have been demonstrated (such as Schottky diodes (Vescan2010) and transistors (Aleksov2003)).

Furthermore the single crystal layers would be better in other applications. The first step toward thatis the deposition of oriented layers

The morphology of layers strongly depends on the growth conditions. The common points of early deposition techniques are the use of 10-100 mbar gas mixture of C/H/(O) which activated by a hot filament or plasma discharge and a substrate kept between 650–950 °C

The theoretical and experimental research which deals with the theory transport processes and reaction of molecules and radicals in the gas mixture, the surface diffusion and growth mechanisms greatly improved the practical deposition process. Our knowledge about the relation of morphology and growth conditions is far from complete. The modification of a developed morphology is practically hard or impossible; therefore it should be controlled during growth. Thus the information should be obtained about the processes during growth. It is getting more obvious that it is necessary to understand better and control the nucleation and growth of diamond in order to further develop the CVD technique especially for single crystal growth and low temperature growth (which would be important for several applications). Morphology of the layer, homogeneity, defect formation or surface adhesion is all affected by the nucleation essentially. The deeper understanding of growth process could contribute to high rate, large area deposition with homogeneous layer and in high quality mass production.

At the Surface Science Lab of the Department of Atomic Physics at BUTE the Ion Beam Mass Spectrometry (IBMS) tool was developed (Kátai1999) for in-situ measurement of the plasma ion composition and energy distribution in the vicinity of substrate during diamond nucleation in a CVD chamber.

Goals

My PhD work has been focusing on the further development of the IBMS equipment in order to contribute to the theory and practice of the CVD diamond growth.

My first goal was based on the idea that measuring the ion energies with the IBMS enables me to control them by adjusting the bias and thus I can avoid or enhance the secondary nucleation. In other words it makes possible to control the texture of the forming layer.

My second goal is related to diamond nucleation. It is based on the observation - coming from the literature and from our system as well - that the nucleation density depends on the substrate temperature. This certainly could be related to the reaction rates of surface processes, however, this also could be related to a different gas composition and ion energy distribution in the vicinity of the substrate. Thus my goal was to investigate the relation between ion energy distributions and the substrate temperature.

Beside the investigation of the nucleation with IBMS I also planned to investigate the growth mechanism of diamond thin films. My main goal was to make the gas composition measurement possible not only during the nucleation phase but in the growth conditions, too. Then I could measure the mole fraction of the different molecules and radicals in the higher pressure range (100 mbar). The IBMS was originally developed for the investigation of the ion composition during nucleation when bias force the ions towards the substrate and the orifice prepared into it. Theoretically the ionization ratio of carbohydrate species could be different in given plasma condition and thus the ion composition is not necessarily same as the real gas composition. It is also not necessary that the change in ion composition is monotonic function of the process parameters. However earlier IBMS measurements strongly suggest this. The ion composition as a function of methane feed measured by the IBMS is very similar to the results of MBMS measurement which uses post ionization (McMaster1995). The similarity of measurement results, which were gained from identical experimental conditions in MBMS and IBMS, give chance to obtain the plasma composition (or at least information on the effect of methane feed) using the IBMS equipment while using the results of MBMS data as a reference. As a result the difference in gas composition in case of higher pressure (100 mbar) compared to lower pressure (25mbar) could be determined.

Experimental methods

The equipment used in the experiments is a microwave plasma enhanced chemical vapor deposition reactor with an analytical tool, the so called IBMS (Ion Beam Mass Spectrometry). Essentially it uses substrates with 10 micron orifice and an ion beam formed out of ions arriving at the surface and getting through the orifice. The beam is led to a quadrupol mass spectrometer and an energy analyzer before detection. Thus the conditions in the vicinity of the substrate can be in-situ monitored during nucleation and growth.

Theses

1. Investigation of ion energies during nucleation

1.a. Using the results of ion energy measurements during the BEN process I have developed a method which enabled to perform the nucleation while keeping the ion energies under the diamond displacement energy and after that diamond was deposited. I have showed that using this technique more homogeneous diamond layer with high nucleation density can be deposited. [1][2][3] [6][7]

1.b. I have found that ion energies depends weakly on substrate temperature in case of bias enhanced nucleation. Thus the dependency of nucleation density on substrate temperature is caused by surface reactions.

2. Development of a novel measurement method and the improvement of the IBMS equipment

I have developed a novel method for measuring the gas composition by in-situ mass spectrometry in the vicinity of substrate during MW-CVD growth which is most appropriate to exactly determine the fraction of metastable radicals. For this purpose I improved the IBMS equipment to be able to operate at 100 mbar pressure range and achieve substantial intensity even at low bias. I have designed and installed new ion optics which significantly improved the sensitivity and reproducibility. [4][8][9]

3. More accurate measurement of gas composition at 25 mbar

Using my novel method I have measured the carbon mole fraction of the different species as a function of the CH_4 ratio in the H_2 feed gas between 0.35 and 8%.

While the most abundant species are the C_2H_2 and methyl radicals (CH_3) in agreement with earlier measurements the amount of C_2H which was not detected earlier by MBMS (McMaster1995) is close to the amount of CH_3 and further radicals have been detected.

Comparing my results to MBMS results the general trends of stable species shows good agreement; however, MBMS increasingly underestimates the ratio of the CH_3 by a magnitude with increasing carbon content. This is due to the recombination of radicals during measurement. My result shows that sum of the amount of the CH_3 and C_2H radicals is comparable to the acetylene molecules. Thus the propriety of growth models solely based on acetylene is questionable. [4][8][9]

4. Measurement of gas composition at 100 mbar

I have succeed to measure for the first time the gas compositon at 100 mbar during CVD diamond growth.

I have found that compared to the 25 mbar experiments where C_2H_2 and CH_3 have the highest intensity arriving at the diamond surface, at 100 mbar the C_2H is the most abundant species, which ratio was increased by 8 times compared to the low pressure case. The growth rate also increased similarly. This confirm the more important role of C_2H in growth. This observation is in good agreement with theoretical calculations which were neglected due to the lack of experimental evidences.[5]

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Outlook

The sophisticated control of ion energies during nucleation could make possible to make more highly oriented or even heteroepitaxial diamond layers. Using bias control technique and electric potential calculations a non-flat structure has been successfully covered with continuous diamond layer (Csorbai2003). Based on the gas composition measurements at vicinity of the surface more accurate models can be established, which could have important role in the industrial optimization of the technology and in high speed deposition. The improved equipment can answer the basic questions of the deposition of nanocrystal and ultrananocrystal diamond. The first results have been reported already (Csikvari2009). Furthermore the equipment can be used in other plasma diagnostic measurement.

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