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Combined AFM–SEM study of the diamond nucleation layer on Ir(001)

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Abstract

During bias enhanced nucleation (BEN) of diamond on iridium the nucleation centres are gathered in discrete islands — the so called "domains". The topographic signature of these domains has been clarified in the present study by two different concepts. First scanning electron microscopy (SEM) and atomic force microscopy (AFM) were combined to take images with both techniques of a small identical area on a standard BEN sample. In spite of the 2–3 nm deep roughening of the iridium it turned clearly out that the surface shows a 1 nm deep depression within the domains compared with the surface of the surrounding layer. On a second sample which did not show the normal roughening the domains could be identified directly from AFM images. The topographic signature of the domains was the same. Conductive AFM measurements showed that inside and outside the domains the carbon nucleation layer behaves like a high resistivity dielectric sustaining fields up to 10^7 V/cm. Finally, the temporal development of the domain patterns was studied by consecutive biasing steps on one sample. Depending on the local ion bombardment conditions we observed lateral growth or shrinkage on the same sample. This result suggests that domain formation is a continuous process during the whole BEN procedure starting from a local nucleation event and subsequent lateral expansion.

Keywords: Diamond growth and characterization; Heteroepitaxy; Bias enhanced nucleation; Iridium

1. Introduction

Providing single-crystal diamond wafers on large areas is one of the main challenges towards a commercial use of diamond for electronics. Nowadays the heteroepitaxial deposition on Iridium (001) via the bias enhanced nucleation (BEN) process [1] seems to be the most promising approach [2]. Several groups with varying concepts for the preparation of epitaxial iridium buffer layers and slightly different deposition setups are working on this topic [3–6]. Common to all is that during the BEN step ions are extracted from a hydrogen/hydrocarbon plasma and are accelerated towards the Ir surface by applying a potential difference of 150–300 V between plasma and substrate. However the features and patterns on the Ir surface after BEN differ considerably dependent on the detailed geometry of the reactor, the activation of the plasma and the exact process parameters. Up to now, a unified picture of the nucleation mechanisms and the structure of the nucleation centres has not been drawn yet.

Fujisaki et al. [5] observed after BEN in a microwave plasma chemical vapour deposition (MWPCVD) setup bright areas in the scanning electron microscope (SEM). In these areas 10–20 nm large diamond crystallites were situated whereas similar dots without an enhanced contrast are found on the residual iridium in between. After a short growth step only the dots within the bright areas grew which confirmed the former interpretation as diamond nanocrystallites. No information concerning the height of these crystallites after BEN could be extracted from atomic force microscopy (AFM) but diamond spots observed by reflection high energy electron diffraction (RHEED) suggest a height of several nm.

Golding et al. [7] studied the pattern on the Ir surface after the BEN process in a MWPCVD setup. SEM images showed block-like bright regions covering most of the surface area which were called a "condensate". Additionally, nanodots with a diameter of 7 nm in a regular arrangement at a distance of 14 nm were observed over the whole surface. Their interpretation as diamond nanocrystallites was recently supported by an X-ray photoelectron diffraction (XPD) study. The XPD data revealed that about half of the surface carbon atoms were situated on crystalline diamond positions [8]. In AFM

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micrographs these nanocrystallites exhibited a relative height of 1–2 nm. It was suggested that the diamond nanocrystallites and their regular arrangement evolved in a self-organisation process out of the highly excited condensate not until the cessation of the BEN process.

In [9,10] a sharpened molybdenum rod was used as electrode to induce diamond nucleation in a microwave plasma. After BEN circular islands with a lateral size of several μm and a height of 2–3 nm were observed by SEM and AFM, respectively. Additionally, particles of 25 nm height were grown on top of these islands.

These islands are very similar to the so called "domains" which we observe as bright areas in the SEM after the BEN step in our MWPCVD setup [11]. Applying a subsequent growth step it was shown that only out of these domains diamond grains start to grow with an extraordinarily high density and epitaxial alignment. This proves that the domains already contain the diamond nuclei or nucleation centres. In contrast to the 2–3 nm high islands mentioned above no significant height contrast could be assigned to the domains in our samples up to this study.

Unlike the aforementioned microwave assisted approaches Sawabe et al. used a direct current (DC) discharge for diamond nucleation [12]. Apart from an increased roughening no definite signature of diamond nuclei was observed in SEM and AFM. In a recent combined XPS and XPD study the size of diamond crystallites was estimated to a few nm in all directions [13].

In the present work we examined the iridium surface after BEN in our conventional microwave setup as well as in a newly installed DC modification. In a first set of experiments the basic problem of an unequivocal identification of the domain areas in AFM measurements was solved in two ways: 1) Combining AFM and SEM allowed to directly compare scanning electron micrographs of domains and the corresponding topographic images at identical spots on the sample. 2) Diamond nucleation and domain formation sometimes occur without roughening of the iridium [14]. On one of these samples the domains could be identified directly from the topographic image. Both concepts yielded a negative height contrast for the domain areas. In further experiments using conductive AFM (C-AFM), the electric properties of the carbon layer inside and outside the domain areas were compared. Finally, the temporal dynamic of domain formation was studied by monitoring the local changes in domain structure in successive BEN steps applied to one sample.

2. Experimental

Iridium films with a thickness of about 150 nm were prepared by e-beam evaporation. $SrTiO_3$(001) single crystals and 40 nm thick films of yttria-stabilised zirconia (YSZ) on Si (001) were used as substrates. Their size was 10×10 mm^2. Detailed process conditions are described elsewhere [15,16]. The mosaic spread of the Ir films was in the range of 0.1–0.2° as measured by X-ray diffraction (XRD) and the surface consisted of large terraces.

For the bias enhanced nucleation of diamond a stainless steel chamber with an inductively heated substrate holder was used. In one set of experiments a microwave plasma combined with a circular anode was used as described previously [4]. The nucleation step typically lasted 60 min at a bias voltage of 250–280 V and a gas pressure of 30 mbar with 7% CH_4 in H_2. During biasing the sample holder served as cathode. The substrate temperature was held at approximately 800 °C.

In a second set of experiments the Ir surface was irradiated with ions produced by a DC discharge in a CH_4/H_2 gas mixture. A copper cylinder with a diameter of 5 cm was placed 2 mm above the sample and a voltage of about +300 V was applied. The CH_4/H_2 ratio and the gas pressure were 2% and 100 mbar, respectively. The nucleation step lasted only 10 min. For this setup a precise pyrometric temperature measurement was not possible.

The samples were characterized by the LEO DSM 982 Gemini SEM which is equipped with two different secondary electron detectors. The annular in-lens (IL) detector is more sensitive to work function differences, whereas the laterally installed conventional type secondary electron (SE) detector is more sensitive to topographic contrasts. In addition, the topography of the samples was quantitatively examined by AFM using the AutoProbe CP Research instrument in non-contact mode.

The C-AFM measurements [17,18] were carried out with a DI Dimension 3100 AFM system (working in air) equipped with a conductive tip and a pA-preamplifier with an overall amplification of 10^{12} V/A. In addition to a conventional deflection mode AFM, a second computer controlled feedback system monitors simultaneously the tip-sample emission current through the films. In this study the tip was biased positively with respect to the substrate. This is advantageous in case of a dielectric layer on the surface because a stable barrier height between the substrate and the insulating layer can be formed [19]. Injection from the tip can lead to erroneous results due to contaminants on the surface. Additionally the electron emission for substrate injection is less affected by the tip geometry.

3. Results

3.1. Topographic signature of the domains in the nucleation layer formed by BEN

To clarify the topographic signature characteristic for the domains we first produced a nucleation layer on Ir/$SrTiO_3$(001) by a 60 min BEN treatment in the MWPCVD setup. After a rough check for the existence of domains by SEM its topography was measured by AFM. These measurements show the typical roughening with 2–3 nm deep grooves [20]. Long range height modulations are also visible but there are no striking features which would allow a clear decision whether domains are present and in which areas of this AFM image they are.

To answer these questions, SEM images of the identical spot with the IL detector are required. Retrieving in the SEM a several micron large area that has been imaged by AFM is nearly impossible without characteristic markers on the surface. Square depressions in the iridium of typically 100 nm lateral