A continuous, seeded H_2/CH_4-molecular beam in support of diamond vapour growth

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The crystallite habit, film structure, and atomic-scale surface morphology of polycrystalline diamond films were analysed for different substrate temperatures, chamber pressures, and CH_4-concentrations. The results are compared to those obtained from films which were grown in support of a neutral, seeded accelerated beam from a supersonic valve for gas inlet. The effect of the beam on crystallite habit and film morphology cannot be explained by a simple cooling of the substrate nor by an increased C-concentration on the surface, and evidence is found that the beam produces an enhanced mobility of the particles on the surface leading to a reduced twin formation rate.

1. INTRODUCTION

Chemical vapour deposition of diamond films with controlled atomic and electronic surface properties is one of the central destinations of current research in this field. It exist a number of different deposition techniques and it is possible to grow films of defined microstructures. However, how the deposition method, gas composition, substrate and gas temperature, and other parameters influence the atomic structure of the surfaces is much less known. And, the major growth species, the molecular processes, and the energies necessary for the chemical reactions discussed in the literature are only speculative. There is a common view, that atomic hydrogen etches unwanted reaction products like graphite or amorphous carbon and that it is important for a transient stabilization of reactive surface sites. These reactions might have energy barriers that can be overcome only by the vapour atoms and molecules of highest energy and, therefore, give reasons for the large amount of hydrogen that is normally necessary in diamond vapour growth. All these aspects of diamond vapour growth suggest experiments in which the kinetic energy of the neutral particles approaching the surface can be increased. A seeded accelerated beam (SAB) of heavy particles diluted in a light carrier gas may be used for this intention - some basic effects of a SAB on the yield of chemical surface reactions are illustrated in [1] and references therein.

In this paper we present some results of experiments in which we used a SAB in addition to hot-filaments to grow polycrystalline diamond films (PCDFs). The SAB is formed by an expansion of a premixed CH_4/H_2-gas (1% CH_4) through a heated supersonic valve. Hereby, the initial thermal motion of the gas particles is converted into a common, directed motion. The H_2-molecules are accelerated to high velocities and drag the few CH_4 - molecules to the same final velocities. Within the adiabatic limit and, e.g., for a valve temperature $T_V = 1000°C$ one obtains kinetic energies for the H_2- and CH_4-molecules of $E_{kin}^{H_2} = \frac{1}{k}kT = 0,4eV$ and $E_{kin}^{CH_4} = m_{CH_4}/m_{H_2} = 3,4eV$, respectively. Here, k is the Boltzmann-constant, T_v the valve temperature, and m the corresponding molecular mass. The kinetic energies of the particles in the beam, although they are surely somewhat lower than the calculated values given above, should be sufficient to influence elemental processes of diamond vapour growth, e.g., to promote the transport of particles onto the substrate, and to stimulate processes at the surface like diffusion, adsorption, chemisorption, and etching.

Characteristics of PCDFs that are sensitive to a variation of such processes are the habit of the crystallites and the structure of the surfaces. The habit is given by the ratio of the growth velocity of the 100-facet to that of the 111-facet, v_{100}/v_{111}, and generally, any change of the growth velocities should also change this ratio (unless the ratio keeps

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accidentally constant). The structure of the surfaces is, e.g., sensitive to the mobility of the particles on the surface; a high mobility produces flatter surfaces than a low one. For a first test of a possible influence of a SAB on the behaviour of diamond vapour growth, we have analysed individual crystals and PCDFs grown with a SAB for gas inlet by scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM). The particular observation of a $(\sqrt{3} \times \sqrt{3})$R30° reconstructed diamond (111) surface has already been published elsewhere [2,3].

2. EXPERIMENTAL

The hot-filament reactor and film deposition are described in [4,5]. For the present experiment, the pulsed high pressure valve used in [4] has been replaced by a heated stainless steal valve. The orifice diameter of the valves used in the experiments was between 20 μm and 40 μm, and the valve was heated by electron bombardment. The SAB was produced by pushing the premixed gas through the hot valve, and it passed two hot filaments before approaching the surface.

The substrates are Sb-doped Si(100) wafers with an electronic resistivity of 0.02 Ωcm. They were separately heated by direct current heating and temperature controlled from the back side by an optical pyrometer (Kleiber 270A, 1 colour, 0.85 - 1.05 μm). Images were obtained with a Zeiss Digital SSM 960 SEM and a Digital Instruments II STM. The STM was operated in air and at room temperature, and the tunnelling tip was cut from a platinum-iridium wire. The tunnelling mode, current I_t and potential U_t of the tip with respect to the PCDF are listed in the figure captions. A positive (negative) U_t means that empty (filled) states of the diamond surface were probed.

3. RESULTS

3.1 Crystal Habit
The habit of the crystallites that forms in the initial growth stage was analysed as a function of the substrate temperature T_s, CH_4-concentration c_{CH4}, total chamber pressure p, and total gas flow Φ. The experimental parameters used to obtain the octahedral, cubo-octahedral, and cubic habit of the crystallites

Tabel 1: Experimental Parameters

habit	octa-hedral		cu.-oc.	cubic			
Figs.	1a	2a	1b 4a 5a 5b	1c	1d	2b 3 4c 5c	4b
T_s [°C]	740	750	820	1.000	950	925	925
c_{CH4} [%]	0,5	1	0,5	0,5	1	1	1
p [mbar]	40	70	40	40	50	50	50
F [sccm]	30	50	50	50	30	30	30
SAB T_v [°C]	no	no	no	no	yes 950	yes 950	yes 500

cu.-oc.: cubo-octahedral
T_s: substrate temperature
c_{CH4}: CH_4-concentration in H_2
p: total chamber pressure
F: total gas flow
SAB: seeded accelerated beam
T_v: valve temperature

visible in Fig.1 are summarised in Tab.1 together with those of all other films that are subject of this paper. The octahedral habit - Fig.1a - developed with T_s = 740°C, c_{CH4} = 0,5%, p = 40 mbar, and Φ = 30 sccm and without using a SAB. A shift to the cubo-octahedral crystallites with near triangular 111-facets - Fig. 1b - was obtained when T_s and Φ were raised to 820°C and 50 sccm, respectively. A further increase of T_s to 1000°C without any other changes of the other experimental parameters leads to the cubic habit visible in Fig.1c. Thus, the habit can be tuned between the octahedral and cubic form by changing T_s between 740°C and 1000°C. In further experiments, we found a shift of the habit towards cubic character as p and c_{CH4} were increased from 40 mbar to 70 mbar and from 0,5 % and 1%, respectively. However, within the investigated range of experimental parameters, the effects of p and c_{CH4} are only weak as compared to T_s.

Now a SAB was used to accelerate the particles approaching the surface. With A SAB from a valve at T_v = 950°C and c_{CH4} = 0,5 % growth of diamond was not detectable. Indeed, we had to increase c_{CH4} to obtain growth of diamond crystallites. Fig. 1d shows crystallites of cubic habit that were obtained with T_s = 950°C, c_{CH4} = 1%, p = 50 mbar, Φ = 30 sccm, and a SAB of T_v = 950°C. Their habit is almost the same
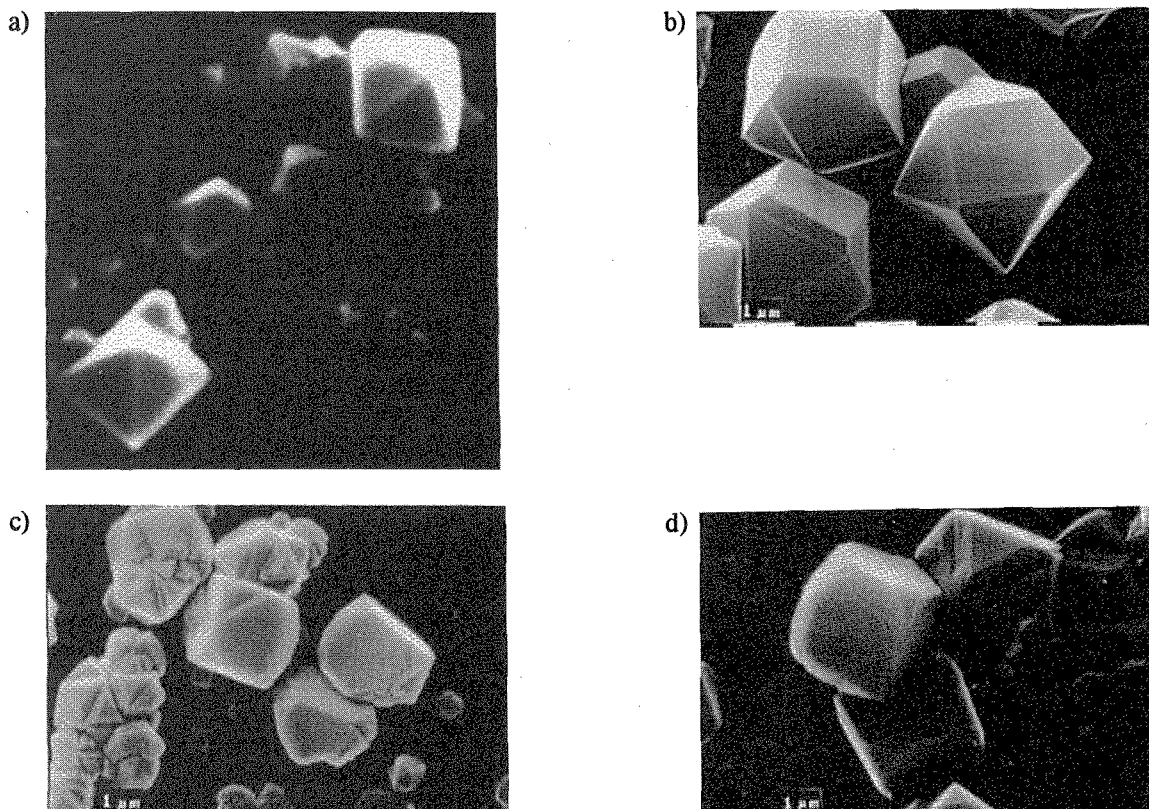
a)

b)

c)

d)

Fig.1: Images of diamond crystallites grown under different experimental parameters obtained with scanning electron microscopy. The experimental growth parameters are listed in Table 1.

as the habit obtained at higher T_S and lower c_{CH4}, and without using a SAB. The habit obtained with the sane experimental parameters but with normal gas inlet is of much stronger octahedral character. From the general influence of T_S, and c_{CH4} on the habit it is quite clear, that the cubic habit found with the SAB cannot be explained by a simple cooling of the substrate due to the beam; In this case, the habit should shift towards octahedral character and not towards cubic character as observed. An explanation of the effect due to an increased C-concentration on the surface is also very unlikely, because in this case a CH_4-concentration of 0,5% should be at least sufficient for diamond growth, which is also not the case.

3.2 Film Morphology
Closed PCDFs being deposited without a SAB exhibit texture formation as expected from the principle of evolutionary selection and twin formation [6,7].

A SEM-micrograph visualising the surface morphology of a film grown from crystallites of octahedral habit ($T_S = 750°C$, $c_{CH4} = 1\%$, p = 70 mbar, $\Phi = 50$ sccm) is shown in Fig.2a. The near 100-textured film with 100-facets nearly parallel to the surface can be explained by the principle of evolutionary selection only, since twin formation is negligible as soon as the surface morphology is determined by 100-facets.

A strong influence of twin formation on the morphology is normally found in closed PCDFs with extended 111-facets at the surface. This has the consequence, that these films show 110-texture independent of their crystal habit. In particularly, in case of a cubic habit, this inhibits the evolution of closed 111-textured PCDFs with extended 111-facets oriented almost parallel to the surface. However, the morphology of closed PCDFs grown with the cubic habit under the influence of the SAB exhibit clear
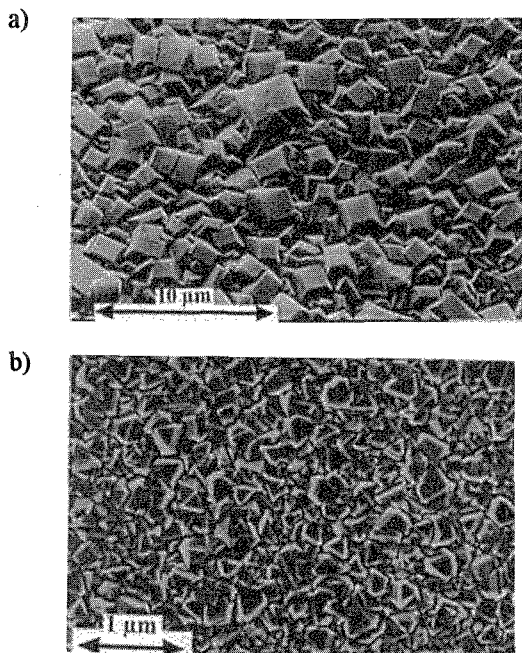
a)

b)

Fig.2: Images of polycrystalline diamond films grown under different experimental conditions. The experimental growth parameters are listed in Table 1. a) A almost 100 textures film. b) A slightly 111-textured film grown with a seeded accelerated beam.

differences. Fig. 2b shows the surface of a film grown under the same conditions as the crystallites shown in Fig. 1d. A lot of 111-facets nearly parallel to the surface are visible which one expects if the film grew after the principle of evolutionary selection and a strongly reduced twin formation rate. X-ray diffraction analysis has revealed a slight 111-texture of this film. An attempt to grow a thick film of pronounced 111-texture by increasing the deposition time failed and Fig.3 shows a cross-sectional SEM-image of the film obtained. A columnar structure is visible, however, there is a clear dark-bright contrast between the material grown in the initial and final stage of deposition. Some of the bright columns expand into the upper half up to the surface. The bright appearing material corresponds to stronger secondary electron emission. Although the reason of this effect is still unclear, such enhanced secondary electron might be explained by a higher defect density of the material grown with a 111-face. Nonetheless, Fig.3 clearly shows a change of film morphology and hence film evolution at an intermediate thickness inhibiting formation of strongly 111-textured PCDFs. A reasonable
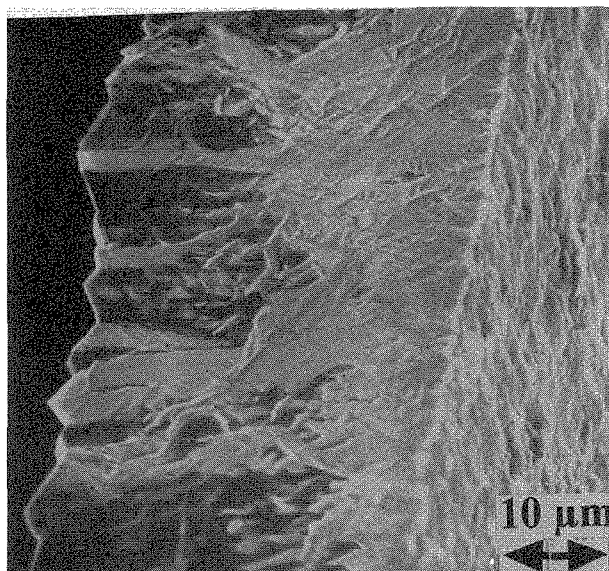

Fig.3: Cross-sectional image of a free-standing polycrystalline diamond film grown with a seeded accelerated beam. Left: growth side. Right: substrate side.

explanation for this effect is the observation, that 111-facets have the tendency to incline with increasing size until 100-facets of twinned crystals appear [8,9]. This effect has been attributed to a limited diffusion of the growth species on the surface. Thus, a consistent explanation for the observed film morphology is achieved, if one assumes, that the SAB reduces twin formation due to an enhanced mobility of the particles on the surface.

3.3 Surface Structure

STM has been used to image the structure of facets on the atomic scale [9,10,11]. An approach of STM to polycrystalline films demands facets oriented almost parallel to the surface, since the surface is otherwise not accessible by the STM-tip. This has the consequence, that a particular facet (100 or 111 in our case) is depictable with a STM-tip only for a restricted range of the experimental growth parameters.

100-faces: Typical STM-images obtained from our 100-textured films exhibit an undulation of the surface on the 100 nm-scale. Until today we were never able to image the crystalline structure of such 100-faces on the atomic scale. The low substrate temperature used for the 100-textured films might result in a very irregular height distribution of atoms on the surface due to a limited mobility of the
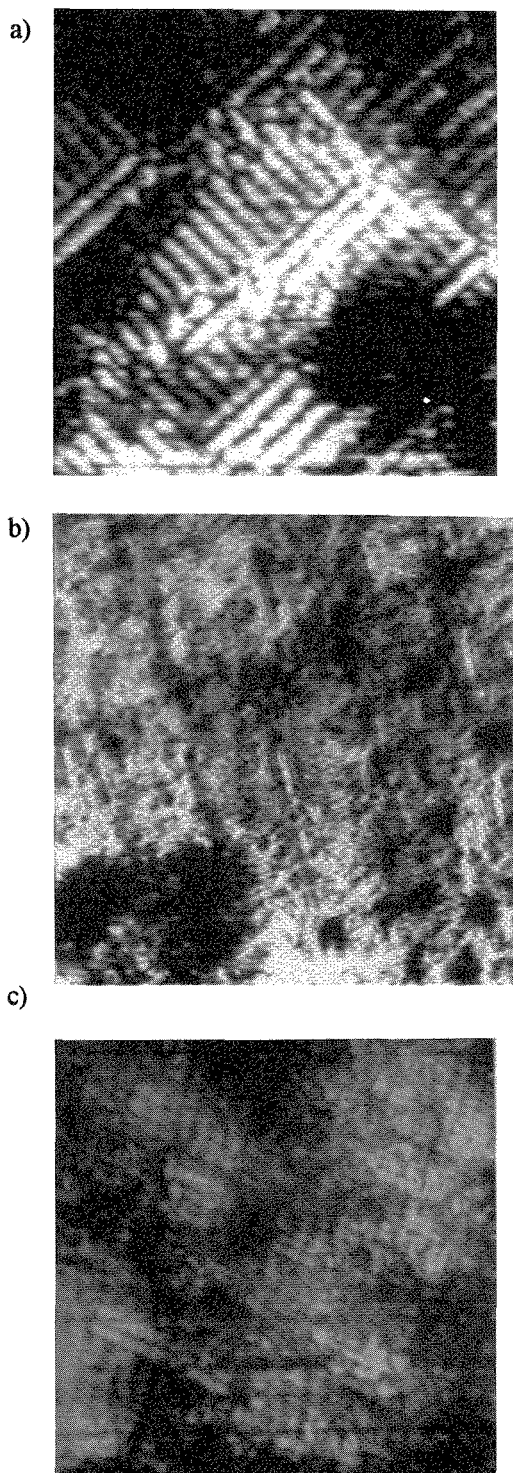
Fig.4: STM-images of diamond (100)-facets. Constant current mode. a):11 by 11nm, Δz=2 nm, U_t=500 mV, I_t=3,2 nA. b):60 by 60 nm, Δz=2 nm, U_t=183 mV, I_t =1 nA. c):14 by 14 nm, Δ =1,6 nm, U_t=400 mV, I_t=1,7 nA.

species during growth or by a thin amorphous overlayer.

When the experimental parameters are chosen such that 110-textured films are obtained, 100- and 111-facets appear at the surface, however, they are tilted with respect to the surface normal. Nevertheless, on films of not fully developed texture, it is always possible to find some facets which are oriented nearly parallel to the surface. Fig. 4a shows a typical atomic scale morphology of such a 100-facet. It depicts a 2x1- reconstructed surface with irregular S_A and S_B-steps [9].

Fig.4b shows an STM-image obtained from a film grown with T_S = 925°C, c_{CH4} = 1%, p = 50 mbar, Φ = 30 sccm, and a SAB of T_V = 500°C. It also visualises a 2x1-reconstructed surface, however, with an extended region (60nm by 60 nm) of stepped single-atomic layers. Such structured surfaces are normally attributed to a non-ideal layer-by-layer growth. However, especially in case of CVD-diamond growth one has to be aware that the surface structure forms by a combination of deposition and etching processes such that the surface morphology might be influenced by either of these two processes.

More extended terraces and thus fewer steps are expected if one, e.g., enhances the mobility of the particles on the surface by increasing T_S. However, on PCDFs grown at a T_S substantially higher than 925°C we were until to date not able to obtain atomically resolved 100-surface structures. An increased mobility of the particles on the surface is also expected if one increases T_V to produce particles of increased kinetic energy. Fig.4c shows the surface of a 100-facet of a film grown with experimental parameters as those used for the crystallites shown in Fig. 1d and the films shown in Figs. 2b and 3. It also shows a 2x1-reconstructed surface, however, the individual dimers within the rows are now clearly resolved. We were not able to obtain a visualisation of the dimers as the closed rows visible in Figs. 4a, 4b by changing the tunnelling voltage at the STM-tip, nor were we ever able to abtain clearly resolved dimers on films grown under conditions as those of the films visible in Figs. 4a, 4b. Consequently, the differences of the images of the dimers are possibly due to different atomic structures [3].

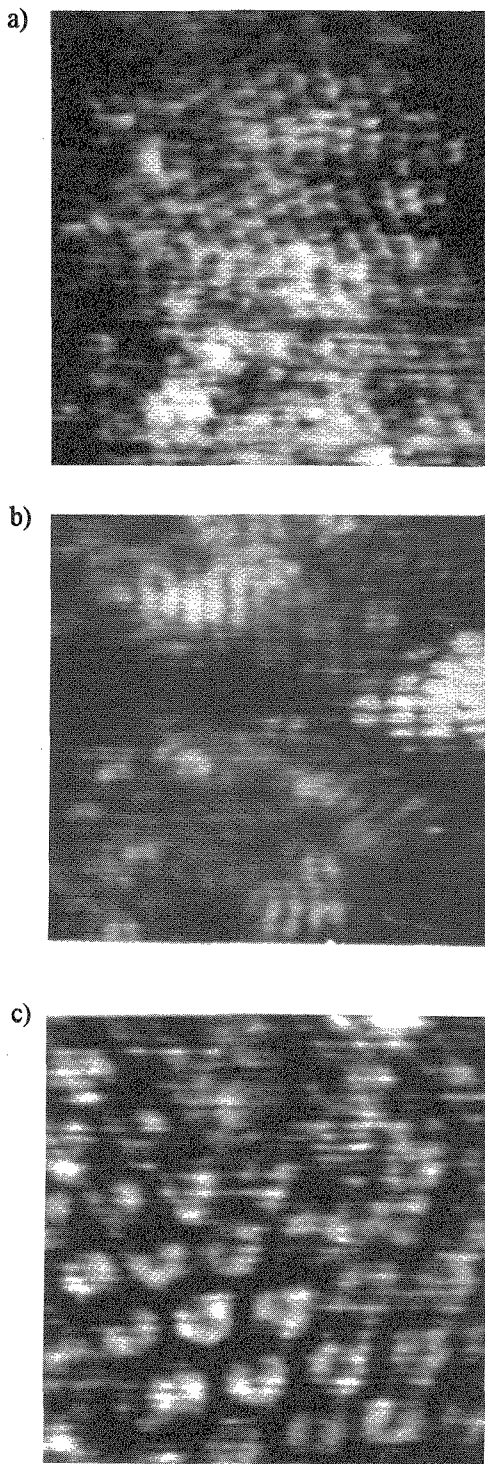*111-faces:* Fig.5a shows an STM-image of a 111-face of an 110-textured film. A six-fold

a)

b)

c)

Fig.5: STM-images of diamond (111)-facets. Constant height mode. a): 4 nm by 4 nm, U_t = -46 mV, I_t = 0,85 nA. b): 4,3 nm by 4,3 nm, U_t = 574 mV, I_t = 1,3 nA. c):14 nm by 14nm, U_t=-48 mV, I_t=0,5nA.

symmetry is visible, with a characteristic spot - spot distance of 0.25 nm corresponding to a 1x1-structure. On the same films, sometimes even on the same facet, quite different structures are visible as it is shown in Fig.5b. Rows are visible with a row - row distance of about 0.21 nm. Three different directions of the rows are observable, which are rotated against each other by 120°. This distance and angular behaviour are consistent with a 2x1-reconstruction of the 111-surface, where in principle at least four different atomic structures are possible /3/.

In case of the slightly 111-textured film grown with the SAB, a $(\sqrt{3} \times \sqrt{3})R30°$ -structure has additionally been observed. On the base of annealing simulations metastable molecular structures have been found [2] similar to the metal-decorated $(\sqrt{3} \times \sqrt{3})R30°$ -structures of other semiconductor (111)-surfaces. The structures may also be described by CH_3-absorption [12], however, the relative high substrate temperature used for our films and the fine structure of the spots [2] give evidence that the structure corresponds to a metastable reconstruction of a complete triple-dangling bond 111-surface rather than to an incomplete CH_3-absorption layer on a single-dangling bond 111-surface.

4. SUMMARY AND CONCLUSION

The habit of the crystallites was varied from the octahedral to the cubic form by increasing the substrate temperature T_s from 740°C to 1000°C. The same tendency was found when p and c_{CH4} were decreased, however, their influence is much weaker. When a SAB with T_v = 950°C was used for gas inlet, a cubic habit was found at lower T_s, higher p, and higher c_{CH4}, as compared to the cubic habit obtained without a SAB.

Without a SAB, the cubic crystallites develop to closed PCDFs of the well known 110-texture that results from the princip of evolutionary selection and a high twin formation rate. With a SAB, 111-texture formation was observed in the initial stage of film formation, which gives evidence for a reduced twin formation rate.

The observed effects of the SAB cannot be explained by a cooling of the substrate (T_s-habit dependence) nor by an increased C-concentration on the surface (no diamond growth with the SAB and c_{CH4} = 0,5%).

There is evidence, that the SAB enhances the mobility of the particles on the surface (reduced twin formation rate). A possible influence of a SAB on adsorption, chemisorption, and etching on the surface cannot be confirmed nor denied here.

STM revealed a variety of different structures on the atomic scale. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ -reconstructed 111-facets and dimer-resolved 2x1-reconstructed 100-facets were found so far only on films grown with a particular set of experimental parameters. This gives evidence that the atomic surface structure of vapour grown diamond as found at room temperature after growth can be controlled by the growth at much higher temperature.

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