Diamond icosahedron on a TiN-coated steel substrate

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Abstract

Diamond layers have been deposited by hot filament chemical vapour deposition (HF CVD) on TiN-coated steel substrates. After deposition, we could observe separate, well-developed diamond icosahedrons and decahedrons on the surface. We have found that a lower content of methane in hydrogen supports their growth, this being a result of multifold twinning. The quality of diamond layers has been evaluated by Raman spectroscopy and scanning electron microscopy.

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1. Introduction

The icosahedron (regular polyhedron with 20 triangular faces) is a forbidden morphology for single crystals. Because of the absence of 5-fold axes in classical crystallography, the external forms of single crystals cannot exhibit such symmetry. However, some ‘crystalline’ objects without three-dimensional periodicity do not comply with this rule. For example, in chrysotile and polygonal serpentine minerals the fibre axis has five-fold symmetry. Five-fold cyclic twins, usually imperfect, have long been known in minerals such as cassiterite (SnO\textsubscript{2}), pentagonite or diamond. Small multiply twinned particles (MTPs) are known with the form of pentagonal bipyramids (decahedrons), and also, rarely, as icosahedrons of elemental metals and of CVD diamond \cite{1}.

For diamond, the three most important surfaces for adsorption and growth are the square (100) surface, the triangular (111) surface, and the less well-defined (110) surface. The measured diamond growth rates on each of these three surfaces depend differently on temperature and on the gas composition. This feature of the kinetics can be used to control the morphology of the crystals obtained, which is characterized by the ratio of the (100) to the (111) growth rates. The so-called \(\alpha\)-parameter is often used to determine the shape of single crystals. This parameter is given by \(\alpha = \sqrt{3v_{100}/v_{111}}\), where \(v_{100}\) and \(v_{111}\) are the growth rates in (100) and (111) directions, respectively. For single crystals, \(\alpha = 1\) for cubes, \(\alpha = 3\) for octahedrons and \(\alpha\) is a value between 1 and 3 for cubo-octahedrons. For polycrystalline films, \(\alpha\) governs the film texture, and by carefully controlling \(\alpha\), smooth films have been grown in which the square (100) surface predominates \cite{2}.

In our paper we report the growth of diamond crystals on TiN-coated steel in dependence on technology conditions.

2. Experiment

TiN coating with a thickness of approximately 300 nm was deposited on steel substrates, parts of a saw blade, by magnetron sputtering. Deposition of diamond layers on TiN-coated steel substrates was performed in a HF CVD reactor.
During deposition, the substrates were mounted on a rotating holder. Three tungsten filaments with diameters 0.7 mm heated to \( \approx 2000 \) °C were placed at a distance of 7 mm above the substrates. Before heating, the filaments had been carbonized in methane atmosphere for 2 h. The gases were admitted to the reactor through a gas shower with a grid. The pressure during deposition was 3000 Pa. The ratio of flow rates of the precursors CH\(_4\) and H\(_2\) during nucleation was 3:300, and during the growth 2:400 (in sccm). The temperature was measured by two thermocouples placed at the margin and in the middle of the substrate. During deposition, the temperature was between 610 and 620 °C. We employed the D-HF CVD (double bias-assisted or dual plasma hot filament CVD) method for nucleation. No other stimulation of nucleation was exploited.

During the nucleation mode, a DC bias of 100 V was applied to the substrate holder. The process time of the nucleation step was 2 h and the time of growth was 8 h.

Raman measurements were conducted in a Raman spectrometer DILOR-JOBIN YVON-SPEX, type LabRam. The excitation source was a He–Ne laser (632.8 nm, 15 mW). The spectrometer was calibrated to the 520.7 cm\(^{-1}\) band of single crystalline silicon and to the 1332 cm\(^{-1}\) line of natural diamond. The measurements were performed at room temperature.

Scanning electron microscope (SEM) LEO 1550 operating in the secondary electron mode was used to study the microtopography of diamond layers and energy dispersive X-ray microanalysis (EDX) was employed for elemental analysis.

Fig. 1. Scanning electron micrographs of diamond CVD grown on TiN-coated steel. The left small picture is a decahedron, the right small picture is a crystallite seen at an angle of 70°.
3. Results and discussion

According to visual observation, all the deposited films are inhomogeneous, the films are not continuous, and contain crystals of icosahedral, decahedral and other morphologies.

Fig. 1 are SEM micrographs of CVD diamond grown on TiN, showing individual diamond crystallites that nucleated in scratches and crevasses on the surface. The pictures show well-developed decahedrons. The decahedron, being observed in our samples rather rarely, consists of 10 (111) facets, five on top and five on bottom, and of five (100) facets completing a pentagonal tube. Fig. 2 shows a crystal of diamond with icosahedral morphology. The icosahedron is of soccer-ball-like shape formed of 20 (111) facets. In Fig. 3 we present Raman spectra taken from three places of the sample. Each spectrum contains the typical ‘finger print’ diamond line at 1332.5 cm$^{-1}$ with a FWHM of 4–5 cm$^{-1}$. Additionally, the Raman spectra contain also the bands of graphite and a broad band centred at about 2257 cm$^{-1}$. This dominant band has also been observed when analyzing diamond films deposited on other substrates such as, e.g. sapphire or WC, deposited in HF CVD and MW CVD reactors.

As a hypothesis, we relate the band located between 2260 and 2270 cm$^{-1}$ to structural defects in diamond layers—twinning. We had previously observed twinning in continuous diamond layers grown in our reactors. As noted by several authors, twinning plays a major role in the growth of diamond films: it affects the morphology and the growth rate [3]. Even the isolated well-developed decahedrons and icosahedrons are probably a result of multiple twinning of diamond crystals. As stated in Ref. [3], a developed icosahedron corresponds to the growth parameter $\alpha=2.3$, and a decahedron to $\alpha=2$. Both types of the MTPs were grown under identical conditions on the same sample. During deposition, MTPs crystalline structures developed also on the TiC-coated steel substrate (see Fig. 4). The parameter which we varied, and which probably affected
the growth of crystals, was the content of methane in hydrogen. This observation is in agreement with the results of other authors [4]. White points on the surface of both samples were analyzed by EDX and are identified as traces of a broken tungsten filament.

4. Conclusion

As proved by Raman spectra from different places of the studied sample, the layers of synthetic diamond on TiN-coated steel substrates are of multiphase nature. We could repeatedly observe the presence of the band at approximately 2260 cm\(^{-1}\) in Raman spectra (or approximately at 740 nm in photoluminescence spectra) of the films with pronounced diamond crystal twinning. The lower content of CH\(_4\) in H\(_2\), 2:400 (0.5%) as compared with 3:300 (1%) in standard growth cycles, did not result in the growth of a continuous film but in the growth of separated diamond single crystals of different morphologies.

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References