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NANOCRYSTALLINE HF-CVD-GROWN DIAMOND AND ITS INDUSTRIAL APPLICATIONS

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Abstract. Nanocrystalline diamond layers with a thickness up to ~ 90 μm have been prepared using the hot-filament chemical vapor deposition technique. These layers show no significant impurities of oxygen and tungsten and exhibit low tensile stress levels < 90 MPa. We obtained a preferential growth in the <110> direction. The estimation of the grain size using the Scherrer formula showed a value of 10 to 15 nm. Finally, potential industrial applications of nanocrystalline layers like diamond coatings of cutting tools and diamond tooth wheels are presented.

1. INTRODUCTION

The correlation between the micro- and nanostructure of a material and its physical and chemical properties is the key issue in materials development. Considerable progress has been achieved recently by the development of new processing technologies (hot filament chemical vapor deposition – HFCVD [1-3]) and new materials in a nanocrystalline state (NCD) with superior mechanical strength and tribological properties [4-6].

Further processes based on lithographic techniques known from silicon technology allow further microstructuring of CVD-diamond. So far, the microstructuring of highly oriented columnar diamond [7] has been hampered by the fact that the internal microstructure is being reproduced by plasma etching yielding rather rough surfaces. This problem now can be overcome by the production of nanocrystalline diamond, i.e. when the grain size is smaller than the acceptable surface roughness. It can be expected that microparts (microtoothed wheels, atomically sharp cutting edges, functionalized diamond surfaces, *etc.*) can be produced on a reliable basis in the near future.

2. EXPERIMENTAL

Nanocrystalline diamond (NCD) films were grown in a CemeCon CC800/Dia hot-filament CVD reactor [8]. Silicon (100) wafers with a thickness of 350 mm and a diameter of 50 μm and 75 mm were used as substrates. In order to achieve a high nucleation density, substrates were treated by a bias enhanced nucleation before film growth. A gas mixture of ~ 3% methane in hydrogen was used as a feedstock gas for growth. Additionally, oxygen was inserted to the gas mixture with a concentration of ~ 1% in order to obtain a nanocrystalline microstructure by preventing cellular growth. Parallel tungsten filaments were electrically heated to a temperature of 1950 °C and served as a deposition source. The substrate

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was heated only by thermal radiation of the filaments to a temperature of ~ 750 °C. The gas pressure was fixed at 5 mbar during deposition. The maximum thickness of the samples achieved ~ 90 μm.

The 4 MV ion accelerator (NEC, model 4UH) at the Lawrence Livermore National Laboratory was used for Rutherford backscattering spectrometry (RBS). The stress measurements were performed by a mechanical measurement of the wafer bending using a Tesa μhite 100 height gauge or by using a Tencor FLX-2908 Thin Film Stress Measurement System. The latter measures the wafer bending caused by the mechanical stress of the thin film using a laser beam, which scans across the film surface and is reflected to a position-sensitive photo detector. By measuring the radius of curvature of the substrate before and after the deposition the stress s in the thin film can be calculated using Stoney's formula [9]

$$\sigma = \frac{Eh^2}{(1-\nu)6(R_2 - R_1)T}, \qquad (1)$$

where $E/(1\text{-}\nu) = 1.805 \cdot 10^{11}$ Pa is the biaxial elastic modulus of the silicon (100) substrate, h is the substrate thickness, T is the film thickness and R_1 and R_2 are the radii before and after the deposition of the thin films, respectively. A Philips X'Pert instrument was used for X-Ray Diffraction (XRD) measurement. For the analysis presented here, we used a standard Bragg-Brentano configuration. An estimation of the average grain size in the films was obtained by application of the well-known Scherrer formula [10]

$$L = \frac{K\lambda}{\beta_{FWHM}\cos\theta}, \qquad (2)$$

where θ and β_{FWHM} are the angle and the full width at half maximum of the considered XRD peak, respectively, λ the wavelength of the used CuK_α X-Rays and K a form factor, which is assumed to be equal to one for our estimation.

For the measurement of the mechanical properties a Hysitron TriboIndenter nanoindentation set-up was used. A Berkovich diamond tip performed the indentation with a maximum load of 250 mN.

3. RESULTS AND DISCUSSION

At the investigation of the hot filament deposition at first the optimum filament temperature T_{fil} has to be established. A high T_{fil} leads on the one hand to an increase of the deposition rate, on the other hand

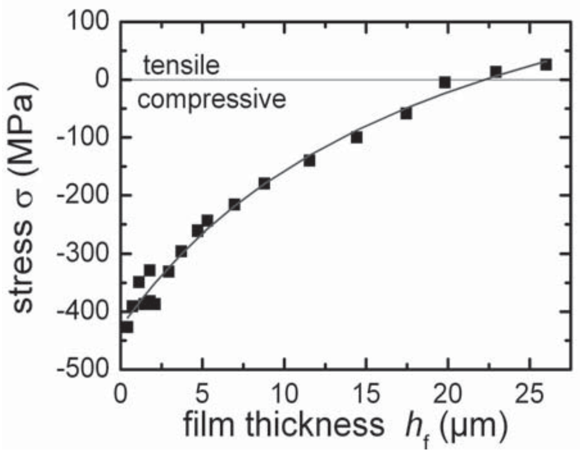

Fig. 1. Mechanical stress σ of the thin film depending of the film thickness h_f.

the crystallize size of the nanocrystals will also be increased. In order to avoid the latter we chose a low T_{fil} compared to other publications [11-18]. The other advantage of low deposition temperatures is the fact that the incorporation of tungsten (W), which was used as filament material, is reduced by low T_{fil}. The investigation of the W impurities in the NCD films using RBS showed that no signals from possible W impurities have been observed, indicating that the W contamination is, if present, below the detection limit of $5 \cdot 10^{-3}$ at.%. Similarly, no oxygen (O) contamination could be detected revealing that the O concentration is below the detection limit of 0.5 at.%.

The analysis of the mechanical properties of the NCD layers showed a hardness of 66.5 ± 0.6 and a Young's modulus of 609.2 ± 3.0 GPa. These values are lower than the values for polycrystalline and natural diamond with 100 GPa and 1050 GPa, respectively.

The NCD films showed no evidence of delaminating from the substrates, suggesting low mechanical stress levels. The measurement yielded tensile stresses of max. 90 MPa for an ~ 80 μm-thick film. Fig. 1 shows the mechanical stress of the thin film depending of the film thickness h_f. At the beginning of the growth the mechanical properties are dominated by compressive stress caused by the interface between film and substrate. When the film gets thicker this compressive stress is overlaid by an intrinsic tensile stress of the thin film. For our deposition conditions these two components compensate each other at a thickness of ~ 22 μm leading to an extremely flat film. For thicker films the intrinsic tensile stress of the film overcompensates the

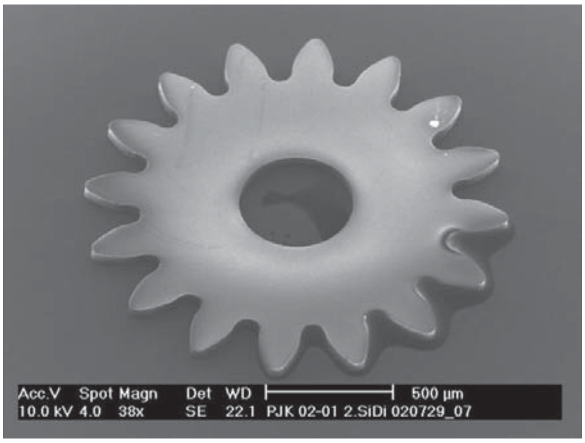

Fig. 2. Scanning electron micrograph of a micro mechanical diamond toothed wheel.

compressive stress of the interface resulting in a low tensile stress.

The XRD pattern of the NCD layers showed peaks at 43.7°, 75.6°, 91.7°, 117.3°, and 141.0° corresponding to the [111]-, [220]- [311]-, [400]- and [331]-orientations of the grains. An estimation of the grain size using the Scherrer formula shows an average grain size of 10 to 15 nm. This value is, however, only a lower limit of the grain size, as the Scherrer formula implies that the peak broadening is caused only by the finite grain size and ignores the broadening by mechanical stress in the layer which however is low.

The grains are not randomly distributed but there is a strong [220]-texture. The ratio of the intensities of the different orientations $A_{111} : A_{220} : A_{311} : A_{400} : A_{311}$ is equal to 84 : 6440 : 3 : 5 : 1. Since 1959 [19], several authors have shown that [110] symmetrical tilt grain boundaries at the diamond structure can grow without broken bonds (for a review and further references see [20]). These grain boundaries are therefore electrically inactive unless activated by impurity uptake. Moreover, from a structural model, which comprises columns of exclusively [110]-orientated nanocrystals, it is evident that no bond length or bond angle distortions occur when building a fully relaxed column. The good mechanical properties of our samples compared with natural diamond as well as the low mechanical stress are in a good agreement with these results.

4. INDUSTRIAL APPLICATIONS

Because of the fact that the NCD show a low residual stress, a high hardness and Young's modulus this material is suitable for industrial applications. In this chapter we present the use of diamond for toothed wheels as an example for micro mechanical parts and the diamond coating of cuttings tools.

Diamond micro mechanical parts. The main advantage can here be taken from the excellent mechanical properties and the low coefficient of friction. Thus, a lubricant-free operation of diamond micro gears at high revolution speed, low wear, low moment of inertia, high efficiency and high reliability is achievable. To evaluate the potential of this application, diamond micro gears have been designed, fabricated and characterized. Fig. 2 shows a Scanning Electron Micrograph (SEM) of a diamond micro gear.

Regarding the small size of the diamond toothed wheels, mounting and adjusting them one to another, leads to problems not known in standard gear production. To enable a sufficient vertical overlap for precise movement, their thickness was chosen to be 150 µm. Even with very high aspect ratio etching processes, a lateral under etch of the mask cannot be entirely suppressed. However, the optimization of the plasma processes allowed the realization of micro structured diamond toothed wheels having sidewall angles of 90° ± 2° at a thickness of 150 mm. As in all plasma structured diamond films, the columnar grain structure reveals again, resulting in a surface roughness of max. 500 nm.

From the toothed wheels, a micro gear was assembled using an aluminum base plate with bores of 0.2 mm diameter for the center axis of each wheel. A nickel-wire of 200 µm diameter was used as axis material. The vertical adjustment of the wheels was realized gluing copings on top of the axis. For actuation, a Faulhaber micro motor series 0206H was used, which was specified to max. 100,000 rpm with a maximum torque of 7.5 µNm. The original output-wheel was replaced by a diamond wheel.

The diamond gear could be successfully driven in this test setup with a maximum revolution speed of 35,000 rpm. After more than 200 min at 20,000 rpm, the gear showed a parasitic destructive breakdown due to a failure of the motor, which was caused by metal particles from the base plate and the axes. A strong wear can be observed after the operation, which is caused by the still too rough diamond sidewall surfaces. The blocking of the gear caused by particles, resulted not in a breakdown of the

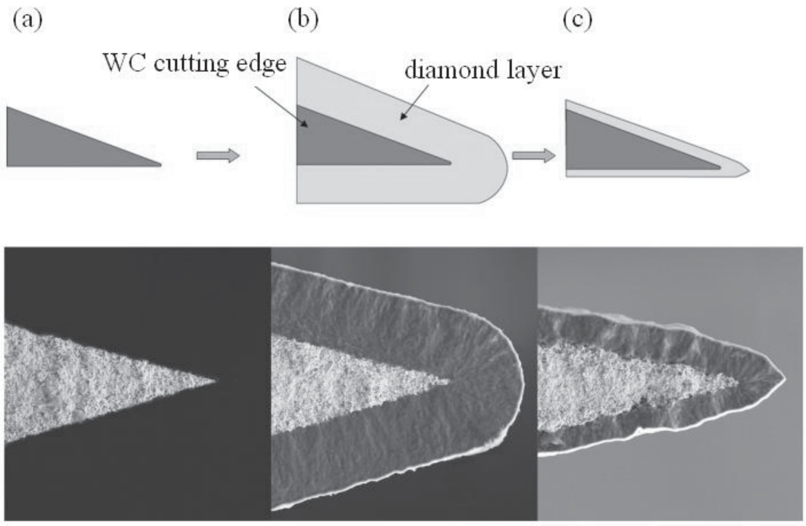

Fig. 3. Principle of the plasma sharpening. After depositing the uncoated tungsten carbide (WC) cutting tool (a) with a NCD layer of the thickness ~ 15 μm the radius of curvature is increased. After etching the diamond layer by RIE from the top side and the bottom side (c) the radius of curvature of the cutting edge is decreased to values even smaller than the original work piece.

wheels, but of the motor itself. Wear of the diamond wheels could not be observed.

Diamond cutting tools. After a chemical pre-treating in order to decrease the cobalt concentration of our tungsten carbide (WC) substrates, we deposited a 10 to 15 μm-thick NCD film onto the substrate. The radius of curvature of the cutting edge, however, increases from an initial value of ~ 1 μm to about 15 μm after deposition. Although the hardness of the tool surface has been significantly increased by the diamond film, the tool is no longer usable since the radius of curvature is too large and the tool is not cutting any more. This is the reason why we introduced a plasma sharpening procedure in order to reduce the procedure. Fig. 3 shows a schematic view of this process. By etching the diamond layer using Reactive Ion Etching from both the top side and the bottom side the radius of curvature of the cutting edge is decreased to values of smaller than 0.2 μm, which is noticeable smaller than that of the original work piece. This process can extend the lifetime of the cutting tool to the factor of 10.

3. SUMMARY

The structural studies of our NCD films deposited using HFCVD revealed that the diamond layer is built up of grains of the size 10-15 nm with a [220]-texture. The films show with a low residual stress, a high hardness and Young's modulus very good mechanical properties suitable for industrial applications. We presented the use of diamond for toothed wheels as an example for micro mechanical parts and the diamond coating of cuttings tools. For the latter we showed a new technique to reduce the radius of curvature of the cutting edge improving the cutting properties and extending the lifetime of the tool by a factor of 10.

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