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Determination of elastic and thermal properties of a thin nanocrystalline diamond coating using all-optical methods

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ABSTRACT

Results are presented on the thermal and elastic properties of a thin, 1.5 μm, nanocrystalline diamond coating (NCD), deposited on a silicon substrate by microwave plasma enhanced chemical vapor deposition. A combination of two all-optical measurement techniques, impulsive stimulated thermal scattering and grating induced laser beam deflection, was employed to launch and detect surface acoustic waves (SAWs). The relation between the dispersive propagation velocity of SAWs to the coating-substrate geometry is exploited to determine the elastic properties of the NCD coating. The elastic properties are found to be consistent with literature values. The thermal properties of the coating were determined by monitoring the thermal diffusion induced washing away of the laser induced transient surface temperature grating. The transient thermal grating signals were fitted by the low-frequency limit of a thermoelastic model for a multilayer configuration. Similar to the dispersion of the surface acoustic wave velocity, the characteristic time of the thermal diffusion driven grating decay evolves from a coating-dominated value at short grating spacings towards a substrate-dominated value at grating spacings well exceeding the coating thickness. The grating spacing dependence of the corresponding effective thermal diffusivity was experimentally determined and fitted, leading to a value for the thermal diffusivity of the NCD coating $\alpha_{NCD} = 8.4^{+2.7}_{-0.1}$ mm$^2\cdot$s^{-1}, which is an order of magnitude lower than that of the silicon substrate. The low value of the thermal diffusivity is interpreted with a simple touching model.

1. Introduction

Natural diamond has several extraordinary properties, such as the highest thermal conductivity and hardness of all known natural bulk materials. However, it is very expensive, rare and from an application point of view it is difficult to incorporate it into miniature devices (e.g. MEMS). Chemical vapor deposition (CVD) diamond coatings might offer a solution for e.g. surface protection and heat sinking [1], provided their properties match the ones of natural diamond. Nanocrystalline diamond coating (NCD) thin films are currently under investigation for material protection and structural hardening in MEMS [2–4], tribological [5,6] and bio-technological [7,8] applications. As the typical size of devices continues to decrease, also the coatings, protecting and serving the application, need to follow this evolution. Typical literature values (Table 1), however, show that the stiffness of artificial diamond coatings with nano-sized grains (NCD) decreases with decreasing coating thickness. This means that NCD looses its protective functional characteristics. Understanding the mechanisms behind the elastic deterioration with decreasing coating dimensions is mandatory to adequately adapt the deposition techniques used in the fabrication of NCD in order to achieve the full potential of extraordinary properties.

Given the very high thermal conductivity of natural diamond and the strong technological need for efficient heat sinking in semiconductor devices from centimeter down to sub-micron scales, there is also a rapidly growing scientific and technological interest in how the effective thermal conductivity of artificial diamond coatings evolves when the thickness is of the order of a few microns or smaller. NCD for industrial applications should be as thin as possible, since the slow growth rate of artificial diamond layers makes their production very costly.

In this work, the focus lies on the determination of the elastic and thermal properties of a thin NCD coating, deposited by CVD on a silicon substrate, by means of laser ultrasonic methods. The first section presents the sample preparation details. The subsequent section discusses the experimental approach and data analysis to obtain the elastic properties of the NCD coating. This work, which extracts information of a rough layer on an anisotropic substrate from the velocity dispersion of surface acoustic waves (SAWs), builds further on a methodology presented in Ref. [15,16]. In the third section a methodology is presented to obtain the thermal diffusivity of the coating based on Ref. [17], where the thermal properties of synthetic diamond coatings were determined by analyzing the evolution of the so-called effective thermal diffusivity as a function of the wavelength of a laser-generated and

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Table 1
Elastic constants of NCD from different sources in literature, appended with results obtained in this work. The acronyms (U)NCD, MCD, PCD stand for (ultra) nano-crystalline diamond, microcrystalline diamond and poly-crystalline diamond. MWPECVD and HFCVD stand for microwave plasma enhanced and hot filament chemical vapor deposition respectively.

Ref.	Material	Growing method	Thickness (μm)	ρ (kg/m^3)	E (GPa)	ν
[9]	NCD	MWPECVD	0.12–1.7	3300–3520	674–953	
[10]	NCD	MWPECVD	0.14		400–1100	
[11]	UNCD	HFCVD	~1	3400–3520	790	0.057
[12]	NCD	CVD	1–5		517–1120	
[12]	MCD	HFCVD	3–4	3400–3530	925–1080	
[13]	NCD	CVD	3.6	3440	1120	0.12
[12]	PCD	CVD	320	3520	1020	
[14]	bulk			3515	1143	0.07
This work	NCD	MWPECVD	1.40 ± 0.04	3250 ± 50	770 ± 26	(0.12)

laser-detected transient thermal grating. Observing the transition from the substrate to the coating regime in the effective thermal diffusivity, results – in analogy with acoustic dispersion – in so-called thermal dispersion. Here both the thermal dispersive behavior, showing an excitation wavelength dependent effective thermal diffusivity of the Si–NCD combination, and a fit of all obtained excitation wavelength dependent experimental data to extract the value of the thermal diffusivity of the NCD coating independently of the Si substrate, are shown.

2. Sample preparation

The NCD film was grown in an ASTeX 6500 series MW PE CVD reactor. The acronyms (MW PE) CVD stand for (microwave plasma enhanced) chemical vapor deposition. Prior to the growth the substrate was pretreated as described elsewhere [18]. Then, to grow diamond, it was exposed to CH_4:H_2 (3:497 sccm of gas flow) plasma for 27 h. The substrate temperature was kept at 575 C° using 3500 W of microwave power and a total gas pressure of 3333 Pa. The in situ thickness monitoring of the growing film was done by analyzing the reflection of a blue laser beam (473 nm) that created interference fringes. The growth was stopped at 1.5 μm NCD thickness. After the growth NCD films surface and cross-section was visualized using a FEI Quanta 200 FEG scanning electron microscope (SEM) (Fig. 1(b)). The NCD coating thickness was confirmed to be 1.5 μm.

As the properties of the silicon substrate are crucial in the determination of the NCD properties from experimental SAW dispersion data, reference measurements were required on bare silicon. For this reason part of the NCD film was removed by reactive ion etching. Half of the wafer was covered with a piece of silicon, acting as a mask, followed by exposure of the non-covered half to an oxygen plasma, which was discharged at 0.5 Pa pressure. The 30 sccm flow of O_2 into the chamber was regulated by a mass flow controller. The sample was placed on a molybdenum stage, which was biased with DC-pulses of 1.6 μs with 250 kHz repetition. The power of the DC-pulses was kept constant at 300 W.

The absorption of the infrared excitation light, see following section, is low for the NCD coating. To enhance the absorption the diamond was coated with chromium. Additionally NCD films typically exhibit an optically rough surface finish (see Fig. 1(b)), which prevents an optimal performance of the all-optical techniques used in this work to excite and detect SAW. To reduce the optical scattering and enhance the reflectivity half of the sample was covered by a 100 ± 10 nm thick chromium layer, using DC-pulsed magnetron sputtering [19]. The resulting sample structure is depicted in Fig. 1(a).

3. Experimental methods

The elastic properties of the NCD coating were estimated on the basis of the measured velocity dispersion data of SAW traveling along the surface of the sample. These waves were excited and detected by a combination of impulsive stimulated thermal scattering (ISTS) with heterodyne detection (HD), see previous work [20], and grating induced laser beam deflection (GILBD), described below. The thermal properties were determined on the basis of the measured thermal decay from the GILBD measurements.

The GILBD setup is an adaptation of an experimental scheme described in [21,22]. Similar to ISTS, a SAW of a chosen wavelength is photoacoustically excited by using a grating excitation setup. However, in GILBD (Fig. 2), the probe laser (cw, 532 nm optical wavelength, 100 mW power) beam is focused by a spherical lens onto on the sample, rather than following the same optical path as the pump laser (pulsed, 1 kKz repetition rate, 1047 nm optical wavelength, 100 μJ/pulse, 10 ps pulse width). The spot size is small compared to the grating spacing so that it is deflected, rather than diffracted as it would be in ISTS, by the thermally and acoustically induced surface ripples. Both the probe laser beam incident on the sample and its specular reflection travel through a quarter wave plate so that the reflected beam is directed off the path of the incident beam by a polarizing beam splitter towards a knife-edging pair of mirrors and finally to a pair of photodiodes (Hamamatsu S5973 for fast detection and S2381 for slow detection, coupled to a Femto high speed amplifier). The detected intensity difference between the two halves of the knife-edged reflected probe beam is proportional with the angular deflection, and thus with the spatial derivative of the normal displacement at the sample surface [15]. The differential signal from the photodiodes was registered by an oscilloscope (Agilent Infiniium 54832 A/B).

The probe spot size was approximately 2 μm. The sample was positioned such that the reflection of the probe beam is uniform and directed back at the detector. Because this is possible GILBD is less susceptible to the sample surface roughness than ISTS-HD. The downside of this technique is that one does not have any knowledge of the location of the detection point with respect to the local maximal amplitudes of the induced grating. It is thus necessary to scan the diffraction grating

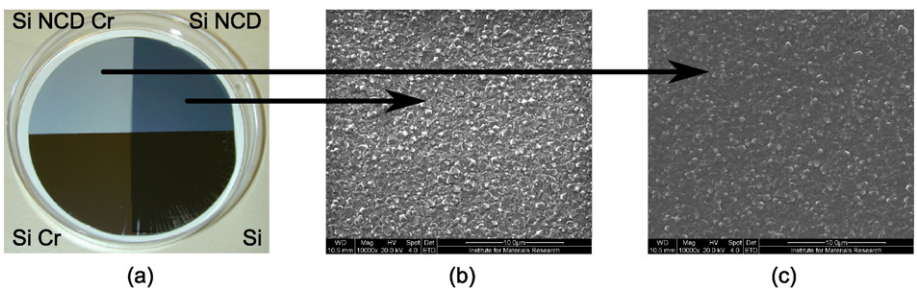

Fig. 1. (a) Configuration of the Si–NCD–Cr assembly. The Si crystal was cut along the (001) plane, the straight cut at the side of the sample marks the [110] direction. (b) SEM image of a 1.5 μm thick diamond film taken on the top left quadrant. (c) The same sample, but covered with a 100 nm layer of Cr. The resulting surface is optically smoother and thus better suited for optical experiments.