

Structuring of diamond thin films by reactive ion etching

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Acronyms

AFM	Atomic Force Microscopy
CVD	Chemical Vapour Deposition
CCP	Capacitively Coupled Plasma
DLC	Diamond-Like Carbon
DI	Deionized Water
FMWP	Focused Microwave Plasma
ICP	Inductively Coupled Plasma
MCD	Microcrystalline Diamond Thin Film
MEMS	Micro Electro-Mechanical Systems
NCD	Nanocrystalline Diamond Thin Film
NEMS	Nano Electro-Mechanical Systems
RIE	Reactive Ion Etching
SAD	Selective Area Deposition
SEM	Scanning Electron Microscope

1 Introduction

1.1 Diamond and its applications

Diamond together with graphite, amorphous carbon, carbon nanotube, graphene and fullerene is one allotropic form of carbon. It can be natural or synthetic. Synthetic diamond films are prepared by high-pressure high temperature (HPHT) [1] or chemical vapour deposition method [2]. Due to its unique combination of properties, such as extreme hardness, high thermal conductivity, wide band gap, negative electron affinity, high mechanical strength, chemical inertness, resistance to particle bombardment and biocompatibility, CVD diamond is a promising material for applications in various fields in electronics, bioelectronics, sensorics, etc [3]. Some potential applications are summarized in Fig. 1.1.

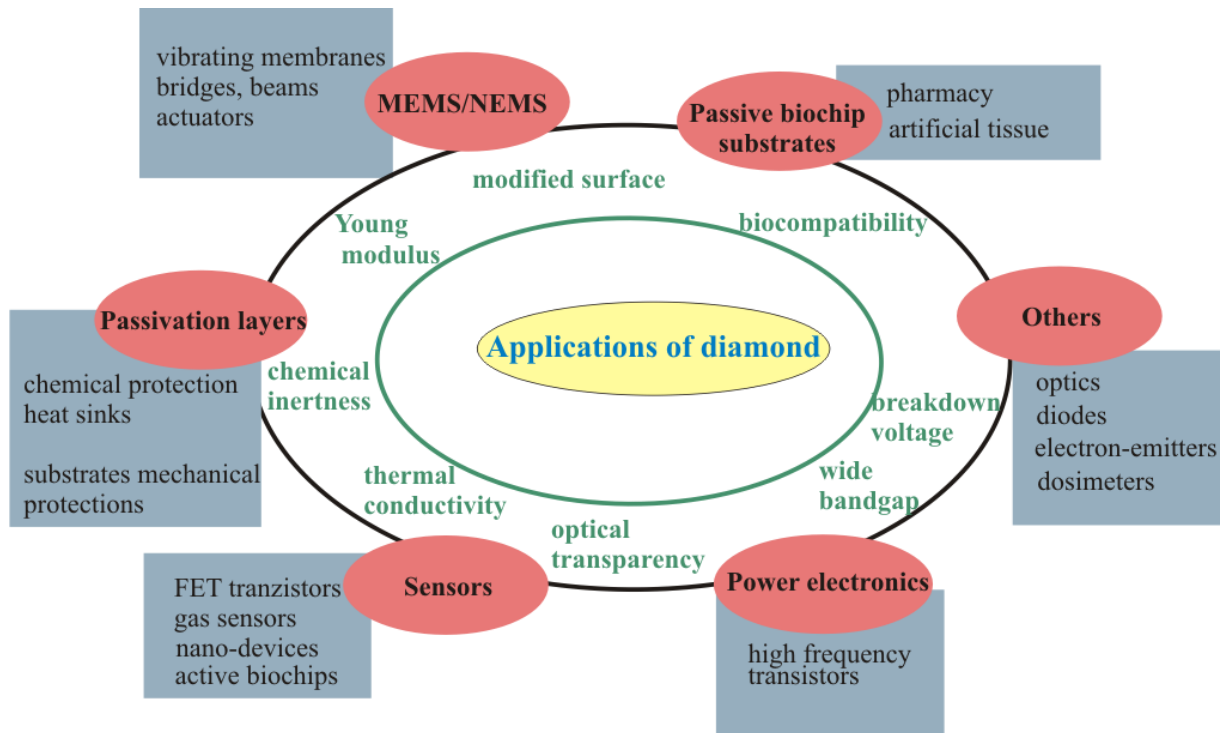


Fig.1.1. Intrinsic properties of diamond and potential applications of CVD films.

The potential application of materials depends not only on their intrinsic physical and chemical properties, but also on the surface geometries in which they appear. The diamond surface can reveal micro- or nanocrystalline grains which consist of sp^3 and sp^2 bonded carbon (carbon in diamond and in graphitic structure). Such a surface can be further modified with atomic/molecular [4] terminations or local charge distribution [5], etc.

Surface modification, i.e. structuring of films, allows wider application of materials, enhances the surface-to-volume ratio and therefore can increase the sensitivity and some other

properties of fabricated devices. For example, increasing the surface area-to-volume ratio of films is relevant to improve the field-emission properties by introducing the enhancement effect of local field near the tips [6], [7]. Structured diamond films are also applied in tissue engineering [8], [9] as DNA chips [10], gas sensors [11], [12], MEMS devices, etc. [13].

Generally, various nanostructures can be fabricated from diamond films, e.g. nanowires, nanorods, nanoneedles, etc. Representative structures and their potential applications are shown in Fig.1. 2. An alternate method to direct diamond film structuring is based on the structuring of the substrate surface before diamond deposition, which can be also useful for specific applications.

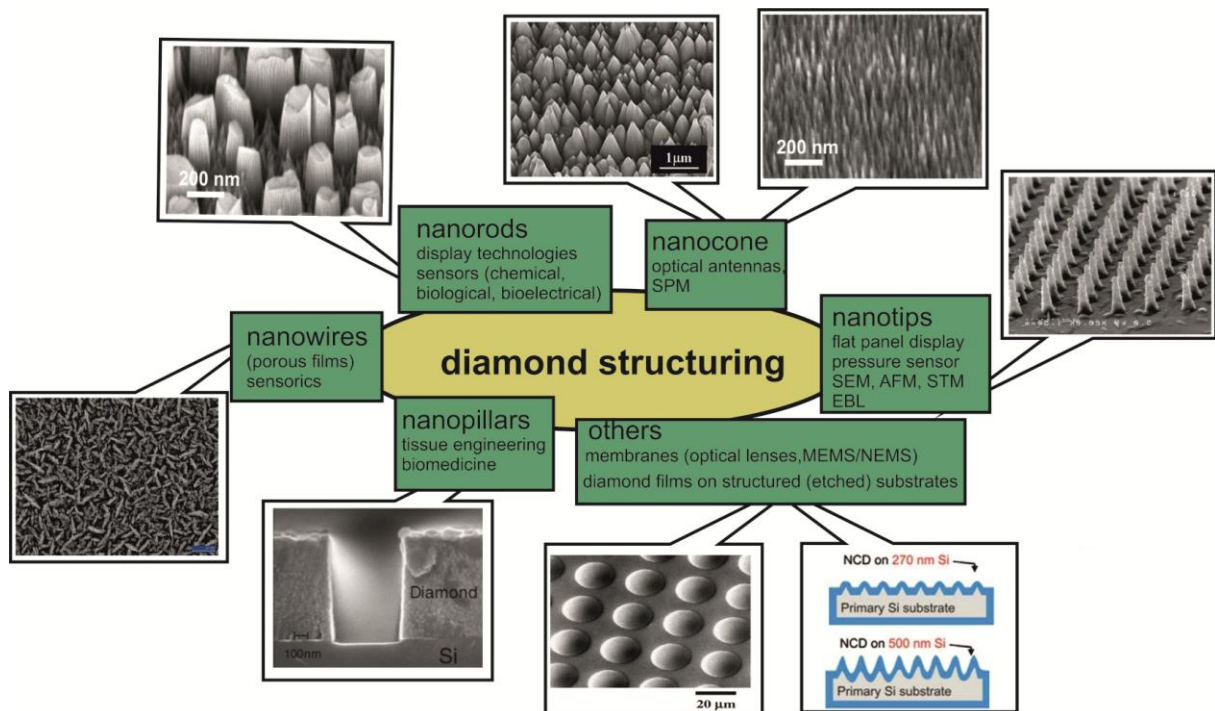


Fig.1. 2. Schematic diagram of diamond structuring and their potential applications [14]–[20].

For achieving controlled diamond surface geometry, the structuring technique has to fulfill several requirements, such as high surface areas, high density of nano-objects, high aspect ratio (depth to width), excellent uniformity over a large area, and process reproducibility.

2 Structuring of diamond

Due to high-temperature stability, super hardness and chemical inertness, it is hard to structurize diamond. Wet chemical etching, which is commonly used in semiconductor industry, is not applicable for diamond; only dry reactive ion plasma etching can be used. According to fabrication or structuring methods, two groups can be defined: a) the top-down and b) the bottom-up strategy.

2.1 Top-down strategy

In Figure 2.1. is shown the schematic diagram of top-down strategies used for diamond structuring. In general, the fabrication of nanostructures requires a masking material to make a desired pattern. The most commonly used masking materials are metals (Au, Ni, Al, etc.), polymers, oxides or nitrides. To achieve the desired structure implementations of several methods can be used, i.e. lithography, imprinting, etc.

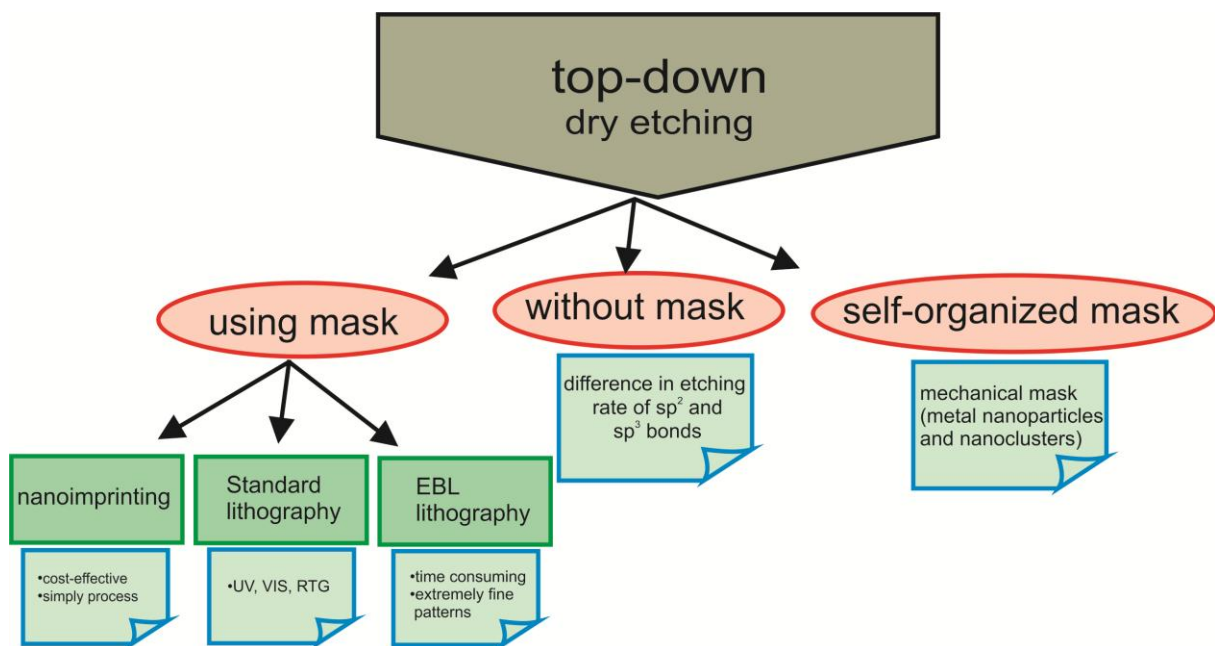


Fig. 2.1. Schematic diagram of selected top-down strategies of diamond structuring.

Lithography is a relatively complicated technological process, consisting of multiple steps: covering of the sample with polymer coating (negative or positive resist), light exposition through pre-fabricated mechanical mask, then development. In the case of etching, additional step, the evaporation of metal film is needed. The minimal size of the structures

fabricated by lithography depends on the type of lithography and the wavelength of radiation used. Depending on the source of radiation it can be [21]:

- photolithography (or optical lithography) - uses visible or ultraviolet light to form patterns on the photoresist,
- X-rays lithography - X-rays (0.4 – 4nm) have much higher energy and much shorter wavelengths than VIS, which allows it to overcome the diffraction limits of optical lithography,
- electron beam lithography (EBL) - is really useful for creating extremely fine patterns without using any mask (with sizes down to 10 nm),
- focused ion beam lithography (FIB) is similar to EBL, with higher writing speed, and does not require a photoresist layer.

However, all of these techniques suffer from certain limitations. In practice, all require a clean room environment. Photolithography does not have the resolution to produce nanometer-scale patterns. X-rays lithography allows high aspect ratio, high penetration and high resolution, but is very expensive compared to photolithography (special masks and resists). EBL can be very time consuming [21].

Another type of lithography is nanoimprinting lithography (NIL), which is a cost-effective manufacturing technology. Compared with conventional lithography, it is a far simpler process (faster than EBL and simpler than X-rays lithography) - it does not use any beams thus it does not require complex optical equipment.

Diamond nanocones and not-organized nanotip arrays can also be fabricated without any lithography and any mask. In this case, the nanostructures are formed due to different etching rate of sp^2 and sp^3 carbon bonds [12]. Sp^3 carbon bonds represent diamond crystals, while sp^2 carbon bonds are characteristic for amorphous carbon or graphitic phases, which are present at grain boundaries or as defects in diamond crystals.

Another simple and easy method of diamond structuring without lithography is based on using a self-organized metal nanoparticles as the mask. In this case, a few nm thick metal layers are evaporated onto the substrate and thermally treated to achieve formation of nanoparticles [22]. However, deep etching of diamond using these self-organized masks is not a trivial task and requires a complex study. The aim is to minimize the cost, time and complexity of diamond nanostructuring.

2.2 Bottom-up strategy

For structuring of diamond film, the usage of the bottom-up strategy is more rare because of the higher complexity and low process reliability. Despite this, several different selective area deposition methods have been invented:

- inkjet printing – a useful technique for direct writing and printing of diamond seeds on the selected area,
- bias-enhanced diamond nucleation (BEN) process on areas pre-defined by SiN or Pt coatings,
- removal of diamond nuclei (seeds) from defined areas,
- SAN (selective area nucleation) – direct nucleation on selected areas
 - diamond seeding using polymer mask and lithographic process
 - using polymer/diamond composite nanofibers.

The bottom-up strategies of diamond structuring are summarized in Fig. 2.2. Selective area nucleation is a novel and perspective method. Combining photoresist, lithography and diamond growth leads to structured diamond film growth without any post-processing. Moreover, it was shown that substrates patterned by polymer stripes (as nucleation layers) play an important role in enhancing diamond nucleation and accelerates homogenous CVD growth at low substrate temperature [23].

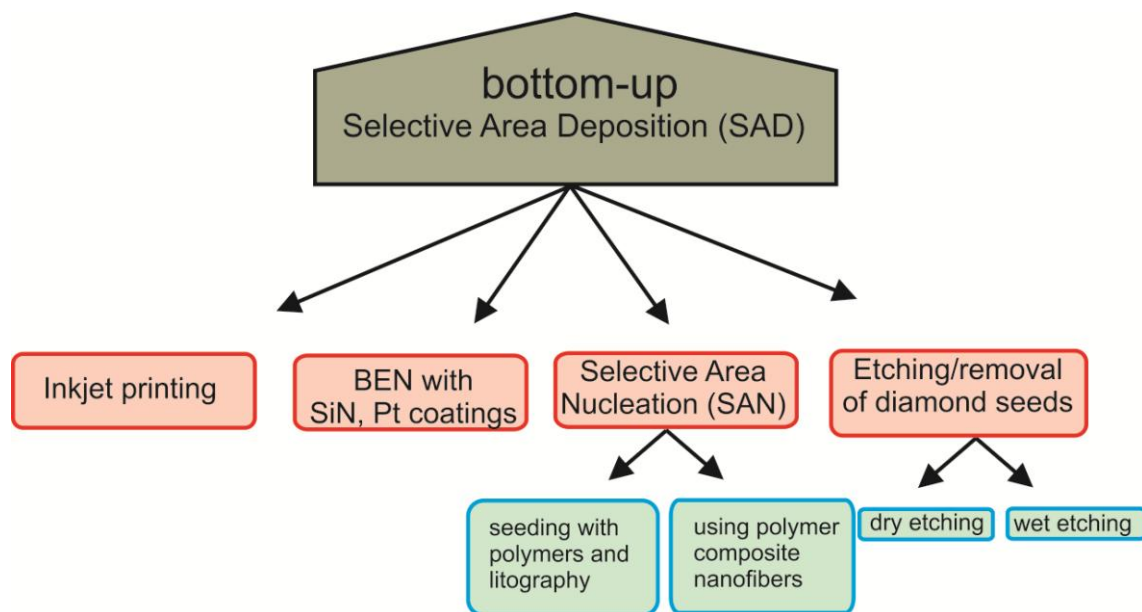


Fig. 2.2. Schematic diagram of the bottom-up strategies of diamond structuring.

In this method, the homogeneous coating of photoresist is achieved by spin-coating. Then the substrate is dried and photolithographically treated to realize requested polymer structure (formation of an amorphous-carbon (a-C) layer), which acts as a carbon source. During the CVD growth some carbon atoms diffuse from the a-C layer to the diamond nanograins where they “feed” their enlargement and continued growth. The implementation of seeding polymer results in the growth of a fully closed diamond layer [24]. It is supposed that the proper combination of the primary polymer with UDD seeding technique can result in a very high seeding density over any substrate material.

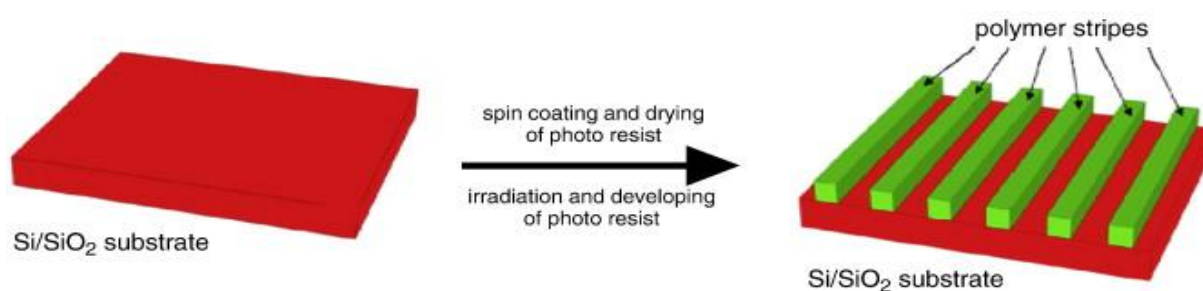


Fig. 2.3. Processing of Si/SiO₂ substrate and formation of the primary polymer stripes [24].

The usage of photoresist and lithographic processes for selective area nucleation was further improved by Babchenko et al. [22]. They investigated SAD of CVD diamond structures applying three different strategies:

(A) RIE - through photolithographic mask

In strategy A, the seeding of the substrate is achieved by ultrasonication in a liquid dispersion containing diamond particles. Next, the samples are covered with a positive photoresist (polymer) by using spin-coating. Optical photolithography is used for photoresist processing. This is followed by a dry etching process which removes seeds from areas not protected by polymer. A schematic illustration of strategy A is shown in Fig. 2.4a.

(B) photolithographic processing - with two polymer layers

First, substrates are covered by spin-coating with polymer (Fig. 2.4b). Then, they are seeded with diamond nanoparticles by ultrasound agitation in a diamond suspension. The seeding layer is covered with a polymer layer and dried. This way, diamond seeds are packed between two photosensitive layers. Preparing patterned structures from such sandwich-like structures requires optical lithography only.

(C) combination of strategies A and B

In strategy C (Fig. 2.4c), substrates are first processed as in strategy B. Finally, they are released by reactive ion etching.

All used strategies result in the direct growth of diamond structures. Strategies A and B show a clear difference in the diamond growth in intended (on-stripe) and unintended (off-stripe) areas. The combined strategy C resulted in the best selectivity of diamond structure formation.

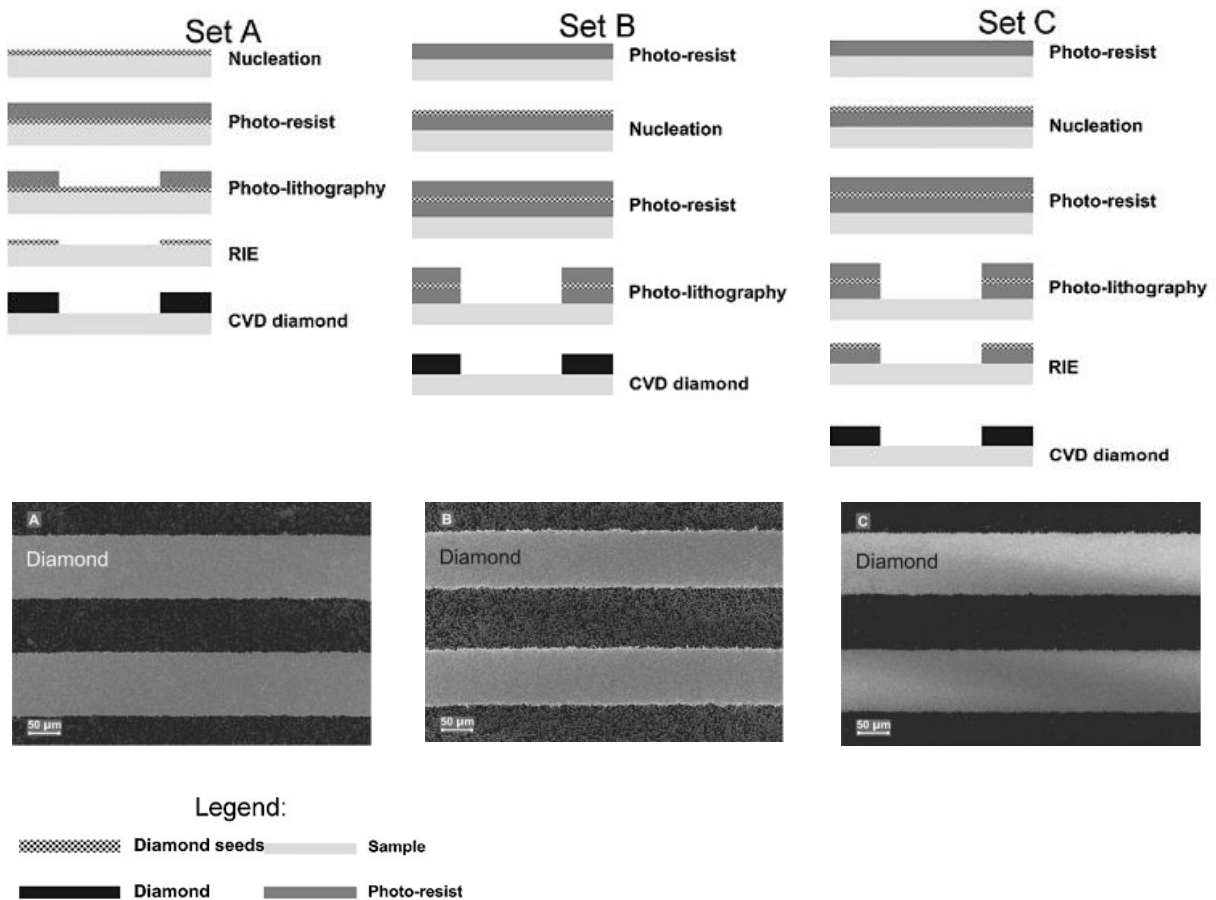


Fig. 2.4. Selective area deposition of diamond using photoresist and lithography with various strategies: a) RIE - through photolithographic mask, b) photolithographic processing - with two polymer layers and c) combination of strategies A and B [22].

The main advantages of all the above described strategies are: (i) omitting any destructive treatment of substrate, e.g., its rinsing in acid to remove metal mask, (ii) easy application on large-area substrates, (iii) suitability for diverse substrate materials and (iv) compatibility with standard semiconductor processes [22].

Another very promising method is the transformation of polymer composite into diamond. In this method the substrates are pre-treated with non-woven composite nanofiber textile composed of poly(vinyl alcohol) matrix and ultra-dispersed diamond (UDD) nanoparticles prepared by needle-less electrospinning method. High concentration of UDD in the PVA fibers leads to the formation of diamond wires due to the combined effect of UDD particles used as seeding and high pressure difference across the fibers interface. Thus, the primary polymer spunbond fibers results in the growth of nanocrystalline diamond structures [25]. Further optimization and improvement of this method should allow nucleation of various 3D substrates over large areas.

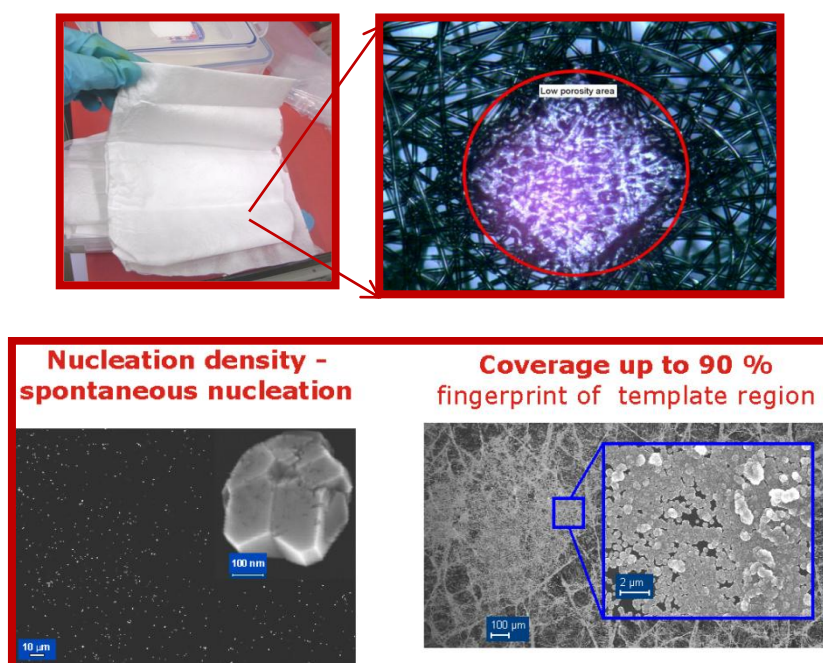
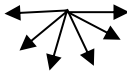
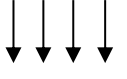


Fig. 2.5. Nanofiber non-woven textile and diamond fiber-like structures [25].

3 Etching mechanism

Etching is a process during which material is removed from selected regions of the substrate by chemical processes or by a sputtering mechanism. In general, there are two types of etching: wet and dry etching. Wet etching uses aggressive acids (such as HF, H₂SO₄, etc.) with good selectivity and high etching rate. Dry etching can be accomplished by applying spontaneous reactions of an appropriate reactive gas mixture without plasma (non-plasma based etching) or with plasma (plasma based etching), and allows short-time processes with high control and reproducibility. More characteristics of both etching techniques are summarized in Table 3.1. [26], [27].

Table 3.1. Comparison of wet and dry etching.

	Wet etching 	Dry etching 
Method	chemical reactions	ion bombardment (sputtering) and/or chemical reactions
Environment	atmosphere/chemical solutions	vacuum
Advantage	low cost easy to implement high etching rate good selectivity	better process control suitable for automation high resolution and cleanliness uses small amounts of chemicals
Disadvantage	wafer contamination issues anisotropy/isotropy differences dangerous solvents	expensive equipment some gases are quite toxic poor selectivity
Directionality	isotropic – leads to undercutting (anisotropic for crystalline substrates)	isotropic and anisotropic

3.1 Plasma etching

In general, plasma etching is a chemical etching, not a physical etching. This means: a chemical reaction takes place between the solid atom and gas atoms to form a molecule, which is removed from the substrate. Because of the existing DC bias voltage, there is always some sputtering. For the large majority of etching processes, this physical etching component is so small it can be neglected. The advantage is that the sample surface is not damaged by accelerated ions.

The etching process can be described as follows: the gases enter the reactor in the form of molecules. In general, these molecules are not reactive enough to react chemically with the sample. A plasma (radiofrequency, microwave, etc.) is needed to dissociate and ionize the relatively stable molecules in order to form chemically active ionic species (radicals). Beside radicals the plasma consists of neutral molecules, electrons, photons, positive and negative ions. In general, there are a million times more radicals than ions or electrons. Ions do not etch, radicals do.

Since the electron mobility is much greater than the ion mobility, after ignition of the plasma the electrode acquires a negative charge, i.e. the DC self-bias voltage. Ion bombardment is caused by positive ions which arrive at the plasma/dark sheath interface and are then accelerated by the negative DC voltage towards the electrode and the wafer placed on this electrode. The transport of reactive intermediates occurs by diffusion. The effect of the ion bombardment depends on the quantity of ions which arrive at the sheath, i.e. on the density of ions in the plasma, and on the energy of the ions, which is determined by the DC voltage [26], [28].

The biggest disadvantage of plasma etching is its extreme sensitivity to many variables. Some of these parameters are well known such as pressure, power, flow rate, etc. However, often the influences such as reactor materials and cleanliness are unintentionally disregarded [26], [28].

In case of diamond, wet chemical etching is not applicable because of its properties (chemically inert, robust, stable and hard material). To date, the diamond is etched using dry reactive ion etching (RIE).

3.2 Reactive ion etching (RIE)

RIE enables profile control with high etching rate and high selectivity due to the synergetic combination of physical sputtering with the chemical activity of the reactive species. Most industrial RIE reactors are equipped with 13.56 MHz radiofrequency (RF) generators, which dissociate and ionize the gas molecules which enter the reactor. The main steps involved in the etching process are: formation of reactive species, adsorption of the reactive particles onto the surface, chemisorption and desorption.

If the energy of the ions is high enough, they can etch the materials without a chemical reaction. This is known as the physical part of the RIE, which is highly anisotropic (i.e. the etching rate is not equal in all directions). In contrast, chemical etching has an isotropic character (etching rate is the same in both horizontal and vertical directions).

Achieving the desired balance between chemical and physical etching is a very complex task, because it is affected by many process parameters [26], [28].

The most widely used RIE etching systems are: capacitively coupled plasma (CCP) inductively coupled plasma (ICP), electron-cyclotron resonance activated plasma (ECR), or their combinations and modifications (see Table 3.1, Fig. 3.1.). The etching characteristics such as etching rate, selectivity, surface morphology, isotropy, reproducibility and uniformity can be calibrated and controlled very precisely with process parameters. Some of their characteristic properties are summarized in Table 3.1.

Table 3.1 Comparison of commonly used RIE systems [29].

	CCP-RIE	ECR-RIE	ICP-RIE
General features	parallel plate reactor – limitation in a configuration for high etching rates at low ion energies RF self-bias voltage forms at the substrate electrode	improved technique of CCP-RIE low energy ion current during the deposition ion current (plasma density) dependent on ECR power	overcome all disadvantage of ECR ion energy (~ self-bias voltage) dependent on the RF power ion current (plasma density) dependent on ICP power
Process pressure	0.7 – 20 Pa	0.06 – 0.7 Pa	0.1– 13 Pa
Plasma density	$1\text{--}5 \times 10^9/\text{cm}^2$	$5 \times 10^{11}/\text{cm}^2$	$5 \times 10^{11}/\text{cm}^2$
Advantages	standard method for the most applications	high rates, low damage independent control of ion energy and ion current density	
Disadvantages	ion energy (~ RF self-bias voltage) dependent on the RF power and process pressure	real wide range fully automatic tuning of the MW energy is difficult very expensive to scale up to large wafer sizes operation outside the resonance (at >0.3 Pa) can lead to MW energy passing to the wafer	limited area

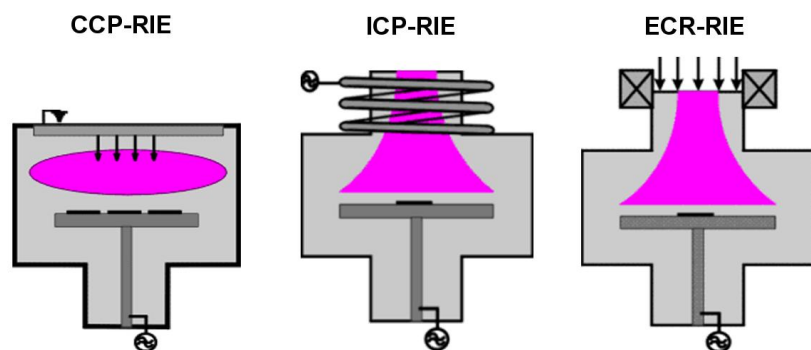


Fig. 3.1. Schematic view of most widely used reactive ion etching plasma systems [30].

3.3 Capacitively coupled RF plasmas

In CCP-RIE systems the RF power is applied to the lower or the upper electrode (see Fig. 3.2.). This generates an oscillating electric field between the two electrodes. Most of them have an operating frequency of 13.56 MHz (above the ion plasma frequency and below the electron plasma frequency). The bulk region of the plasma is partially ionized by the discharge and is semi-neutral (nearly equal number of electrons and ions). Sheath regions form automatically near the electrodes to keep the plasma neutral. The mean free path of ions is considerably shorter than that of the electrons, which reach the reactor walls and electrodes much faster than the ions. The ions cannot follow the applied field because of their large mass. The electrons however are accelerated by the RF field and charge the capacitor (a resistor and a diode connected in parallel) negatively. This leads to a negative self-bias voltage on the electrode, which repels the electrons and accelerates the positive ions. They arrive at the plasma/dark sheath interface across the sheath and are then accelerated toward the self-biased electrode (through a maximum potential of $V_p + V_{dc}$), where they bombard the substrate [26].

The main limitation of capacitively coupled RF plasmas is the direct coupling of the plasma density to the ion energy. To obtain a high density of reactive particles, the power in the plasma must be increased [26].

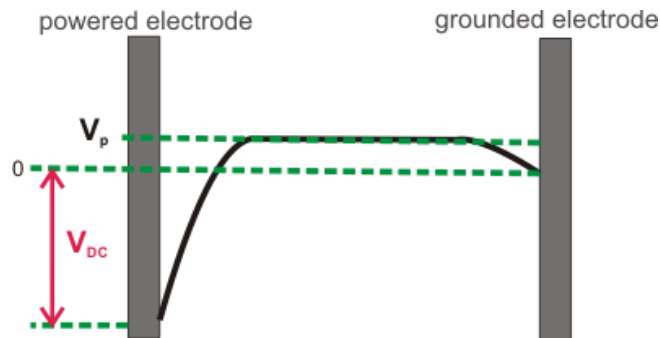


Fig.3.2. DC voltage in the plasma reactor in RIE mode.

4 Experimental part

The experimental part will focus on the structuring of diamond films using a top-down strategy. Reactive ion etching techniques were used and the influence of etching parameters (gas mixture, pressure, power, etc.) on the etching rate and diamond film properties were studied. In addition, we studied the structuring of substrate material (i.e. polished silicon wafer and glass substrate) in order to obtain structured diamond films without further processing after diamond deposition. Several mask materials were used and compared:

- (i) evaporated continuous metal films (Ni, Au and Ti/Ni),
- (ii) self-assembled metal particles (Ni, Au),
- (iii) simple mechanical mask (piece of Si wafer),
- (iv) no mask (differences in etching properties of sp^2 vs. sp^3 carbon bonds).

Grown and etched samples were characterized by profilometer (Dektak 150), Scanning Electron Microscope (eLine writer, Raith), Atomic Force Microscope (Veeco Dimension 3100, NTMDT Ntegra) and by Raman Spectroscopy (Renishaw inVia Reflex Raman microscope with excitation wavelengths NIR/VIS/UV). The results are discussed below in chapter 5.

In general, the process of fabricating diamond nanostructures was carried out using the following fundamental steps:

- 1) growth of diamond film (nucleation and deposition),
- 2) mask preparation (metal evaporation and/or thermal post-treatment in case of self-assembled metal nanoparticles),
- 3) reactive ion etching.

Fig.4.1. shows a schematic illustration of the main technological steps in the case of using self-assembled metal nanoparticles as masking material.

4.1 Diamond deposition

4.1.1 Nucleation

Nucleation and seeding (or substrate surface pre-treatment) is necessary to enhance the formation of diamond nuclei on non-diamond substrates (such as Si, glass, etc.). Without a

nucleation process diamond films cannot be grown on non-diamond substrates, or they grow very slowly. There are many nucleation methods such as scratching [31], ion bombardment methods, coatings by amorphous carbon layer [23], etc. Ultrasonic seeding with diamond particles in suspension with DI water was used [29]. First, prior to the nucleation process, the substrates were treated by our standard cleaning process: 15 min in isopropyl alcohol and ultrasound bath, washing in DI water, and then ultrasonically nucleated in suspension of DI water and ultradispersed detonation diamond (UDD) powder in diameter 5-10 nm. Finally, they were dried by nitrogen.

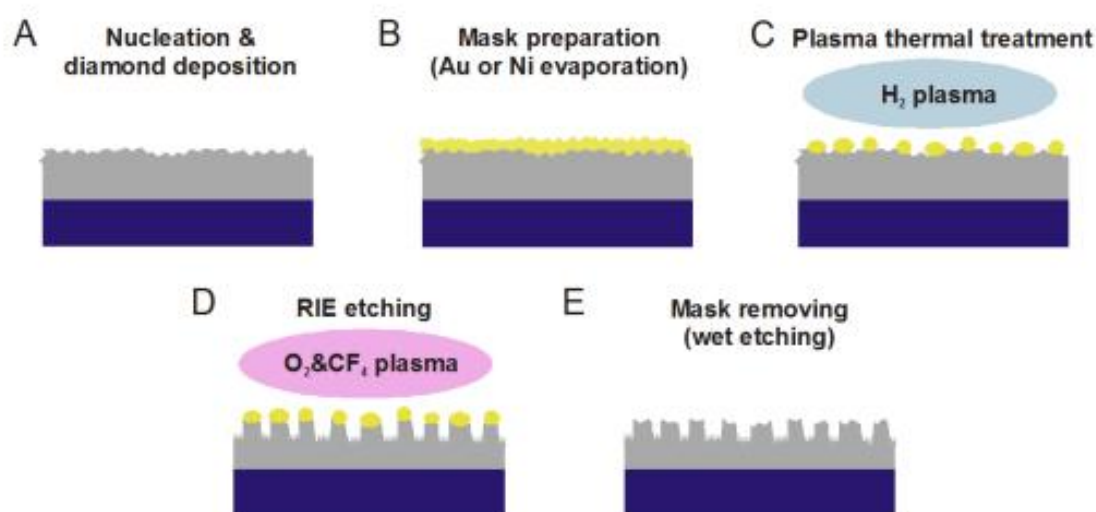


Fig. 4.1. Illustration of the technological steps of diamond nanorods fabrication using self-assembled metal nanoparticles as masks [29].

4.1.2 Growth

Several studies have reported that the final diamond surface after identical etching conditions strongly depends on the properties of diamond films (morphology, structure and composition), which are fundamentally different due to their difference in grain sizes, grain structure and bonding character [16]. Therefore, it is recommended to study the etching process for all types of diamond films (single-, polycrystalline, micro-, nanocrystalline or porous diamond films). Hence, in the present work the etching process of diamond films with different morphology of micro-(MCD) and nanocrystalline (NCD) character was studied.

The diamond thin films were deposited on seeded Si substrates in focused microwave plasma (FMWP) CVD system (Aixtron P6) under different conditions for nano- and microcrystalline diamond film, summarized in Tab. 4.1. Three different deposition sets were

performed in aim to prepare a thick diamond layer (their thicknesses and corresponding roughnesses are summarized also in Tab. 4.1.). The first set was used for basic study of the etching of diamond films using various masks, while sets 2 and 3 were used to compare the influence diamond crystallinity (MCD vs. NCD) on their structuring

Tab.4.1. Summarized deposition parameters.

	Set 1 (MCD)	Set 2 (MCD)	Set 3 (NCD)
Power	3000 W	3000 W	3000 W
Pressure	10 000 Pa	7000 Pa	7000 Pa
CH₄/H₂ ratio	1.5%	5%	2%
Other gases	-	1.5% CO ₂ to H ₂	1% N ₂ to H ₂
Temperature	950°C	890°C	800°C
Deposition time	5 h	2 h	2.5 h
Thickness	~ 2 μ m	~ 1 μ m	~ 1.1 μ m
Roughness	~ 180 nm	~ 100 nm	~ 20 nm

Fig.4.2. and 4.3. show the morphology of diamond films as observed using SEM and AFM microscopy. Microcrystalline diamond film consists of large diamond crystals with size of 400-600 nm in diameter. Films from large crystals reveal high surface roughness (~100-200 nm). In contrast to MCD, nanocrystalline diamond film has a smaller grain size (under 50 nm), its surface morphology is more similar to diamond-like carbon (DLC) films with very low surface roughness (~50 nm).

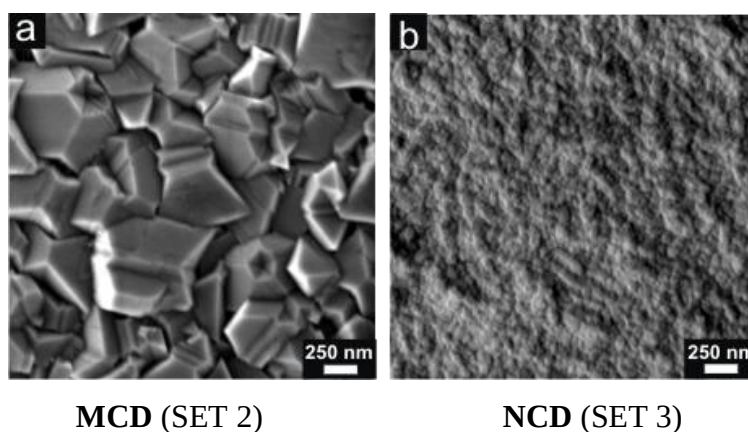


Fig. 4.2. SEM images of deposited (a) micro- and (b) nanocrystalline (b) diamond thin films (note: the SEM images of Set 1 are nearly identical to Set 2).

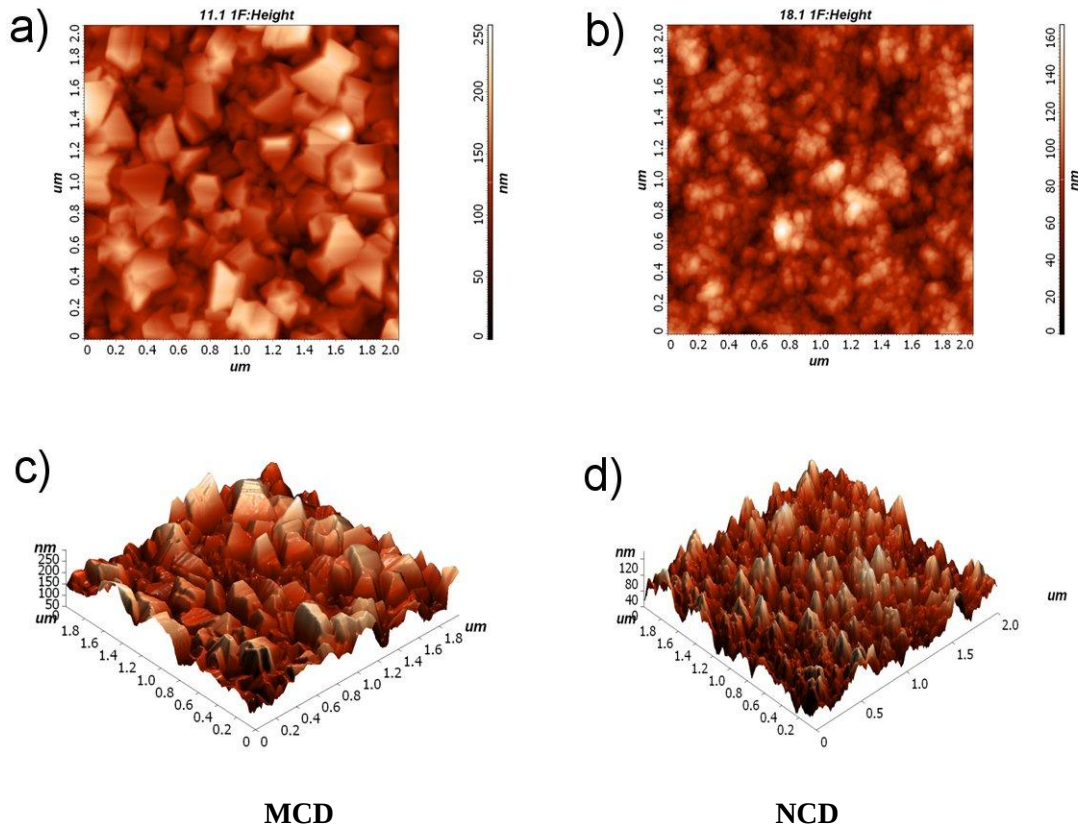


Fig. 4.3. AFM images of the micro- (a) and nanocrystalline (b) diamond films with their 3D image representation (c, d).

More information of carbon hybridization of MCD and NCD films are arise from Raman spectroscopy measurements (Fig. 4.4.). The Raman spectrum of MCD film shows a sharp line at 520 cm^{-1} which is attributed to the Si substrate, then a sharp peak located at 1332 cm^{-1} , which is characteristic line for the phonon mode of the sp^3 crystalline diamond phase. It is also labelled as the diamond peak. Other bands in the Raman spectra are the D- and G-bands, assigned to the non-diamond carbon (sp^2 bonds). The D-band (disordered graphite-band) is located at frequency of $\sim 1374\text{ cm}^{-1}$, and the G-band (graphite-band) at frequency of $\sim 1575\text{ cm}^{-1}$. There is one additional band at $\sim 1154\text{ cm}^{-1}$, which corresponds to trans-polyacetylene-like groups at grain boundaries, and also is often used as the signature of nano-crystalline diamond character. This band is more intensive for NCD films, where the crystals are much smaller, and more sp^2 carbon bonds are present at grain boundaries. Therefore, the intensity of the G-band increases and the intensity of the diamond-peak (at 1332 cm^{-1}) decreases (Fig. 4.4.b).

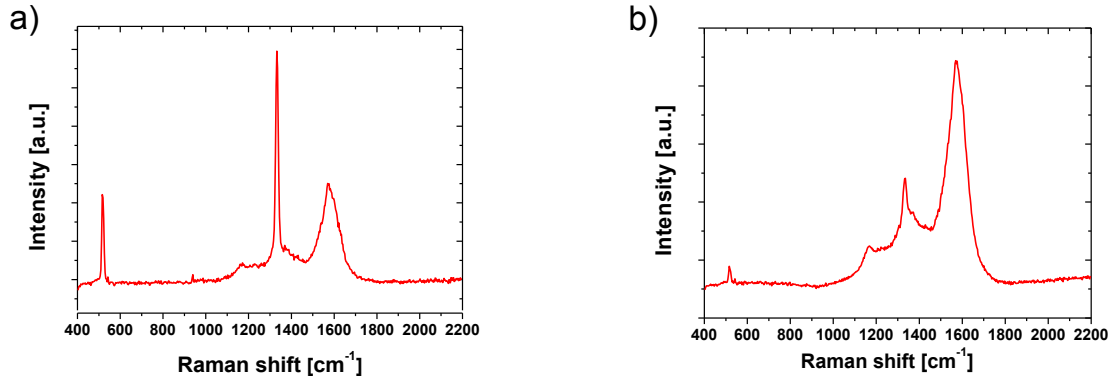


Fig. 4.4. Raman spectra of MCD and NCD films measured by excitation wavelength of 325 nm.

4.2 Mask preparation

First of all, it can be noted that the etching mask must have several basic properties:

- side wall protection from emitted electrons - minimization of mask undercut,
- stable under the optimized etching conditions,
- high selectivity (i.e. ratio of the etch rate for the target material and mask is high),
- easily removable mask after etching process.

The mask materials were chosen based on these requirements. Continuous film of (i) Au, (ii) Ni and (iii) Ni/Ti was evaporated with thickness of > 50 nm (max. 70 nm). For nanorods fabrication, self-assembled metal nanoparticles mask was also used. In this case, a few nanometres thick metal film was evaporated on diamond film (3-15 nm of Au or Ni), then thermally treated in hydrogen rich plasma for 10 min at a temperature of 500°C to form single metal clusters with required diameters (see Fig. 4.1.). The advantage of a metal etch mask is that it can be removed using wet chemistry. However, it has a severe problem with undercutting. The diameter of metal particles depends on the thickness of the evaporated metal layer, and their statistical distribution shows Gaussian-type behaviour. For the thinner metal layer (2.8 nm) the droplets were quite similar in size (i.e. 30-40 nm in diameter), while with increased layer thickness the droplets size distribution was getting broader (in the case of 15.2 nm thick Au layer, the diameter of the droplets varied from 350 nm to 500 nm) (see Fig. 4.5.).

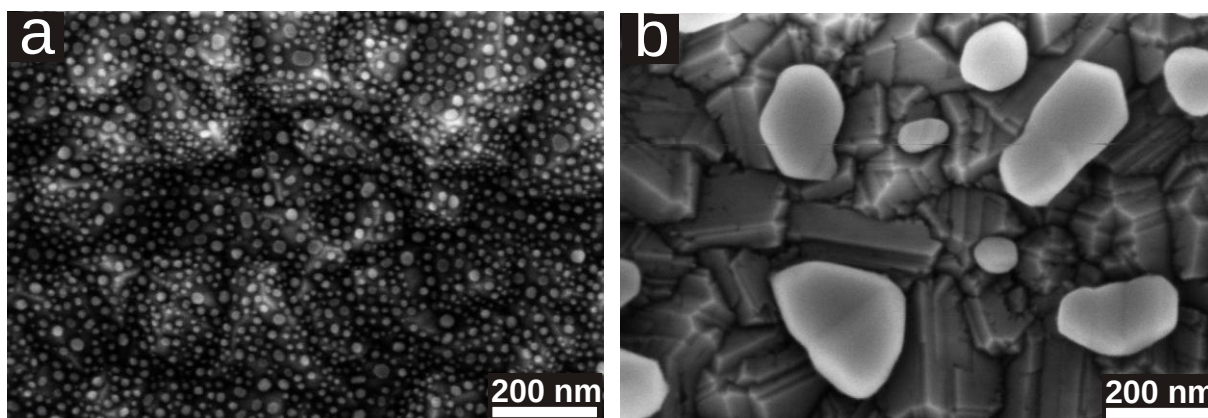


Fig. 4.5. SEM images of the self-assembled metal particles for (a) 2.8 nm (labelled as “small” mask) and (b) 15 nm thick Au metal layer (labelled as “large” mask) after thermal processing in hydrogen rich plasma used for diamond film structuring.

4.3 Etching

The samples were etched in a capacitively coupled reactive ion etching (CCP-RIE) plasma system (Phantom III, Trion Technology). The CCP-RIE system consists of two electrodes suitable for industrial application (6“ wafer etching). The lower electrode is approx. 20 cm in diameter (Fig. 4.6.). The other specifications of the RIE system are listed in Tab. 4.2.

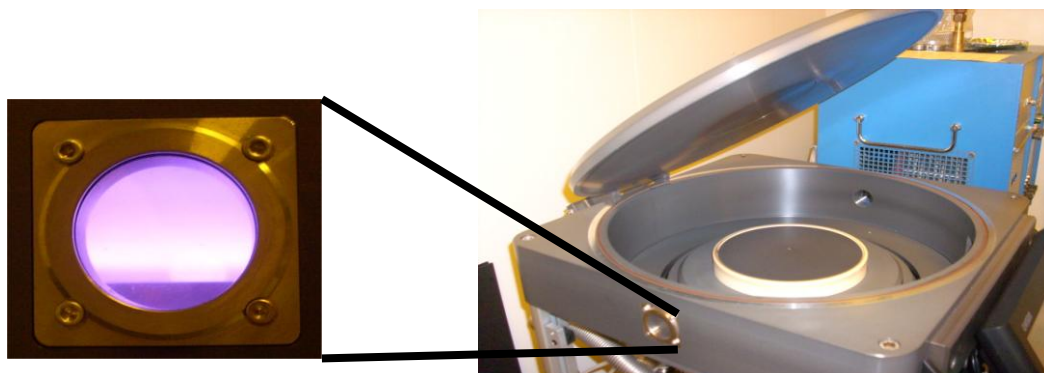


Fig. 4.6. CCP-RIE system Trion Technology Phantom III. The picture on the left illustrates the plasma colour during the etching process with CF_4 and O_2 .

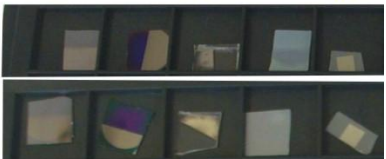
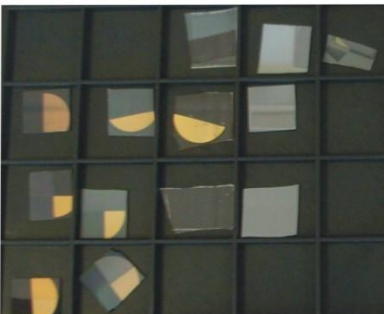
Tab. 4.2. Specifications of the CCP-RIE system.

RF power	13.56 MHz; 0-600 W
Gas inlet lines	5-50 sccm; O_2 , CF_4 , SF_6 , N_2 , Ar

For diamond etching, the most commonly used etchants are: oxygen (O_2), argon (Ar), and carbon tetrafluoride (CF_4). We also studied the influence of these gases on diamond

etching, as well as the influence of SF₆ and their combination. The used gas mixtures are summarized in Tab. 4.3.

Tab.4.3. Gas mixtures used at etching process of samples (MCD, NCD, glass, Si, SiN and PMMA) and their eye-view after etching.

Sample	SF ₆ [sccm]	O ₂ [sccm]	CF ₄ [sccm]	Ar [sccm]	Bias voltage [V]	
						SiN PMMA Glass Si MCD 
A	-	-	45	5	-30	
B	-	5	45	-	-8	Glass Si MCD 
C	25	25	-	-	-6	
D	25	-	-	25	-10	
E	25	-	25	-	-15	
F	26	-	-	-	-8	
						NCD MCD Glass Si 
G	25	-	-	25	-200	
H	25	-	25	-	-5	
I	-	-	2	48	-102	
J	-	48	2	-	-65	MCD NCD Glass Si 
K	-	50	-	-	-61	
L	2	48	-	-	-60	
M	2	-	-	48	-61	
N	-	25	25	-	-58	

Note: the other etching parameters were the same for all samples (except for one): RF power 100 W, pressure 12 Pa, etching time 10 min. Only for sample G was the power 500 W.

5 Results and discussion

5.1 Mask material

As first findings, the mask material is discussed. As we mentioned above, one half of samples were covered with a piece of Si substrate to make a reliable mechanical mask, and in some cases a metal layer was also evaporated to investigate its stability. It was observed that the etching mask (continuous Au, or Ti/Ni layer) was partially or entirely destroyed after etching (for example see sample I in Tab.4.3.). This means the mask material used for etching must be carefully selected regarding to etching conditions (high ion or electron bombardment). We used gold as mask material because it is a standard material in electronics (lithography, electrical contact pads, etc.), but it is more expensive than other metals. Unfortunately, it has bad adhesion on glass, same as other metals, and therefore thick metal layers are prone to peeling away from the glass. Nickel and titanium is well known to have good adhesion to silicon, but Ni is hard to evaporate in our system because it diffuses to the holder, from which it is evaporated. This problem can be solved by evaporating Ti onto the Ni layer, but Ti forms a Ti carbide layer through a solid state reaction at the diamond/Ti interface and it is very hard to remove it (nearly impossible). In the future, a possible solution could be using an electroplated Ni layer with a thickness up to a few micrometers.

5.2 Etching rates & surface morphology

A detailed SEM and AFM study of the etched profiles combined with the surface profilometry data and optical reflectance measurements were used to evaluate the surface morphology, roughness and etching rates. The etching depths of samples (described in Tab. 4.3.) are summarized in Tab. 5.1. As it is shown, several samples were difficult or impossible to measure. It was either due to high surface roughnesses (in case of MCD), or hard material (glass), or unsuitable etching conditions. Also, the etching depth data measured with various methods (AFM, profilometer and optical reflectance measurement) differ, which make our results questionable. For example, in the case of MCD films, the AFM and profilometer measurements did not measure any etching depth, while we were able to detect some etching depth values by optical reflectance measurement. In the case of NCD films, the AFM measurements also did not measure anything, while using a profilometer was more successful

and optical reflectance measurements also worked correctly. In the case of Si substrate and glass, we supposed that profilometer measurements showed more correct data, than AFM measurements. We suppose that the measured area has a big influence on the differences between profilometer and AFM data – while profilometry is performed on a long line scan (2-5 μm or more), it is more accurate than AFM measurement, which is done on a much smaller area (500x500 nm^2 , or 1x1 μm^2). Optical reflectance measurements also provide valuable data, because they are independent on the interface position – only the measurements on etched and non-etched large surfaces are compared.

Tab.5.1. Summarization of etching depth evaluated by different methods.

	MCD		NCD		Glass		Si	
	Optical measurements[nm]	AFM [nm]	Profi-lometer [nm]	Opt. meas. [nm]	Profi-lometer [nm]	AFM [nm]	Profi-lometer [nm]	AFM [nm]
A	NA	NA	NA	NA	90 (20 min)	NA	230 (20 min)	NA
B	NA	NA	NA	NA	97 (20 min)	NA	250 (20 min)	NA
C	NA.	NA	NA	NA	86	25	10	1200
D	NA	NA.	NA	NA	NA	NA	12	3600
E	NA	NA	NA	NA	NA	30	12	617
F	NA	NA	NA	NA	NA	21,8	11	NA
G	NA	NA	NA	NA	800	432	360	3200
H	71	NA	64	17	NA	NA	104	1000
I	140	116	70		NA	108	86	16,8
J	NA	NA	NA	291	NA	NA	NA	NA
K	NA	NA	113	269	NA	NA	NA	NA
L	NA	NA	120	130	NA	NA	150	15
M	NA	156	244	200	130	45	2600	1000
N	NA	270	54	167	NA	NA	530	300

NA- not available

As an illustration, some AFM images of samples were selected and are shown below. Fig.5.1. shows the top-view of glass and Si samples at interface etched in Ar/SF₆ gas mixture (G). On the right are their calculated etching depths from AFM data. In the case of glass,

AFM data show 471 nm etching depth, while profilometer measurements evaluated 80 nm. A bigger difference was observed in the case of Si substrate: according to AFM the etching depth is 3.2 μm , while for profilometer it is 10 times less (0,36 μm).

By etching not only the depth profile of samples can be changed, but also the surface roughness. Surface roughening is shown in Fig.5.2. on glass and Si substrates. In this case a gas mixture of CF_4 and SF_6 was used. A 45 nm etch depth was measured by AFM microscopy for glass substrate. But as we can see on the AFM image, the etched region looks more rough than the non-etched area. Probably due to CF_4 some polymer structures were formed. This layer has a big influence on glass properties such as transparency and reflectance.

AFM images of the MCD and NCD films at etched and non-etched area interface are shown in Fig 5.3. As we mentioned earlier, the etching depth of MCD films is hard to measure with AFM microscopy due to the high surface roughness.

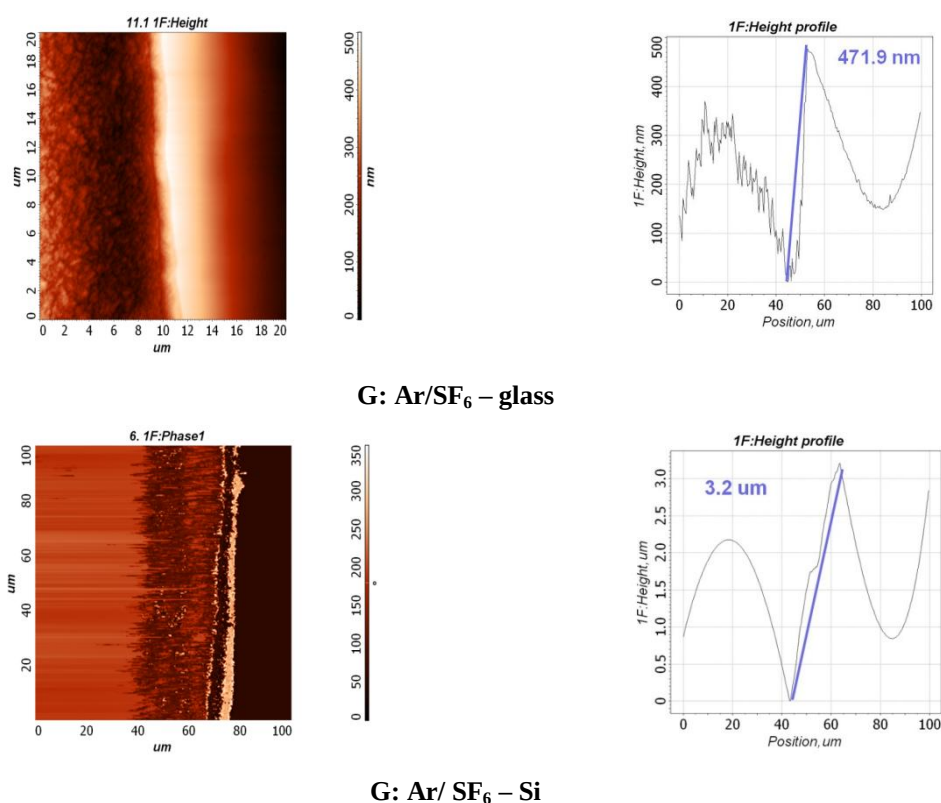


Fig. 5.1. Representative AFM images of the glass (upper row) and Si substrate (bottom row) at interface (left side is the etched area, right side is the non-etched area), and their etching depths (sample name: G).

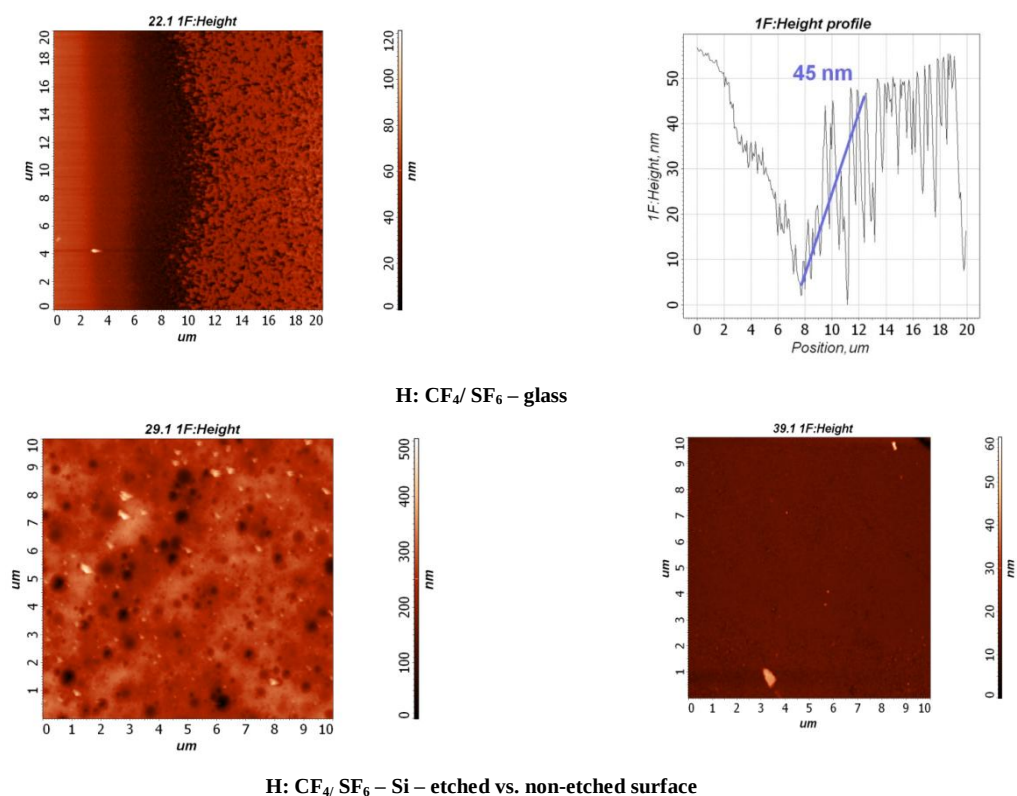


Fig. 5.2. Representative AFM images of the glass (upper row) and Si substrate (bottom row). (sample name: H). In case of Si substrate the etched (on the left) and non-etched area (on the right) is shown.

In the case of glass the surface roughening is observed.

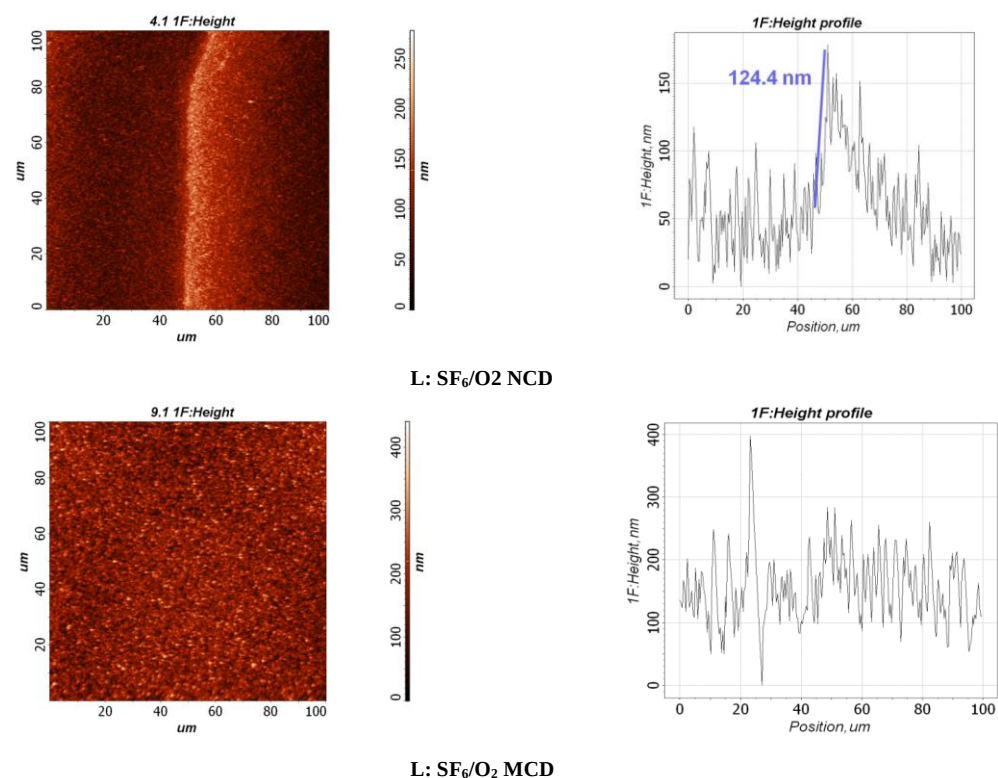


Fig. 5.3. AFM images of the glass (upper row) and Si substrate (bottom row) at interface (left side is the etched area, right side is the non-etched area) and their etching depths.

Another method, which was used for etching depth measurement, is a Dektak surface profilometer. Its measured behaviour for Si and glass substrate is shown in Fig. 5.4.

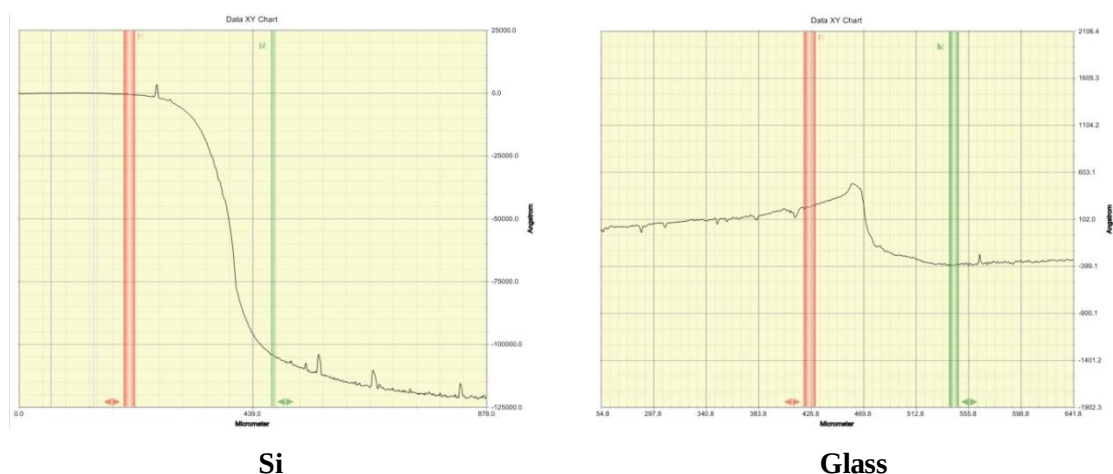


Fig. 5.4. Representative profilometer measurements by Dektak 150 profilometer for Si (on the left) and glass substrate (on the right). Etching depths: 10 μm for Si, and 65 nm for glass.

As a third method, optical reflectance measurement was used for etching depth confirmation. The reflectance spectra of the samples were measured in visible and near infrared regions using the IR-Plan Advantage Spectra-Tech microscope (space resolution 100 μm) equipped with a 20W tungsten halogen lamp as a light source and BWTEK BTC112E TE Cooled CCD array spectrometer (spectral range 400–1000 nm). The diamond films thicknesses were evaluated from the interference fringes in the reflectance spectra applying commercially available Film Wizard (Scientific Computing International) software. The principles of thickness evaluation are described elsewhere [32]. Representative line from optical reflectance measurements is shown in Fig. 5.5.

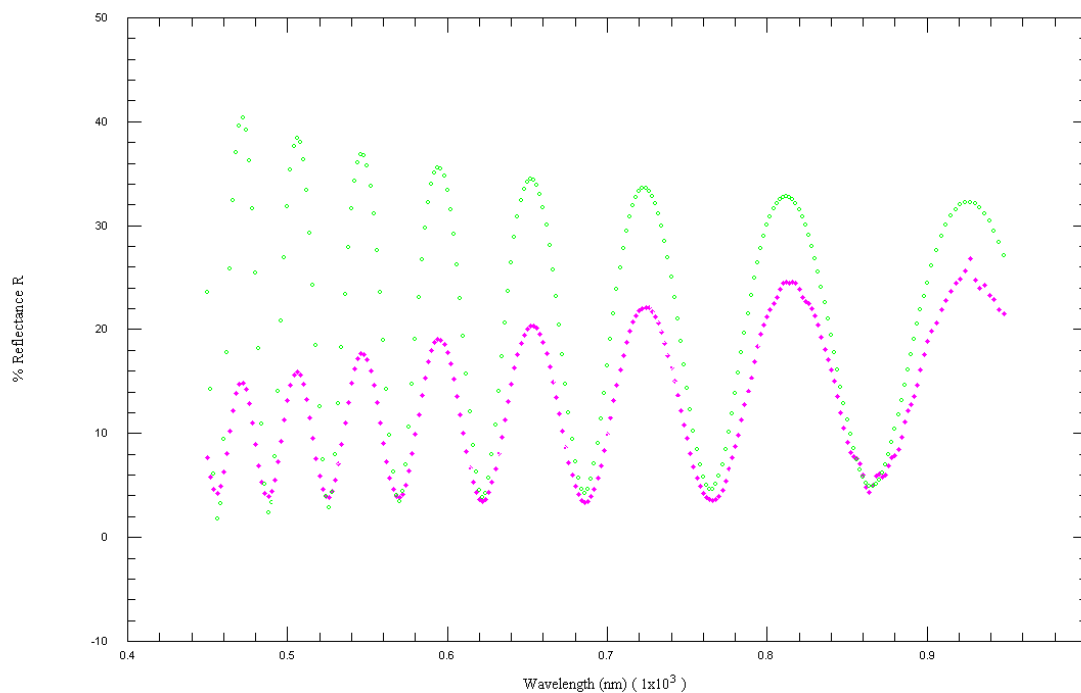


Fig. 5.5. Representative optical reflectance measurement data with fitted behaviour in Film Wizard software for sample J, NCD.

(Green line: measured behaviour, purple line: fitted behaviour)

5.3 Results & discussion of Si and glass etching

We also tried cross-section SEM microscopy to confirm the etching steps of the samples, but without any appreciable results. The steps were not observed even for the 10 μm etching depth measured by profilometer. Only the top-view images were appreciable. Fig. 5.6 shows the top-view SEM images of glass and Si substrate etched in Ar/SF_6 plasma (sample G). In general, SEM microscopy of glasses is not a simple task because of the charging of the surface by electrons. This leads to the floating of the picture as shown on Fig. 5.6c., or on the image in the middle, when the interface between etched and non-etched areas is shown. The etched surface area of the glass substrate shows some change in morphology, as well as some surface termination because of the bright SEM image in comparison to the non-etched area. The effect of surface charging can be minimized by evaporation on thin metal layer. In the case of Si substrate, the difference in morphology between the etched and non-etched areas are much more noticeable. Non-etched area features a smooth surface, while on the etched area polymer-like stripes are observed. This could be due to the SF_6 gas used.

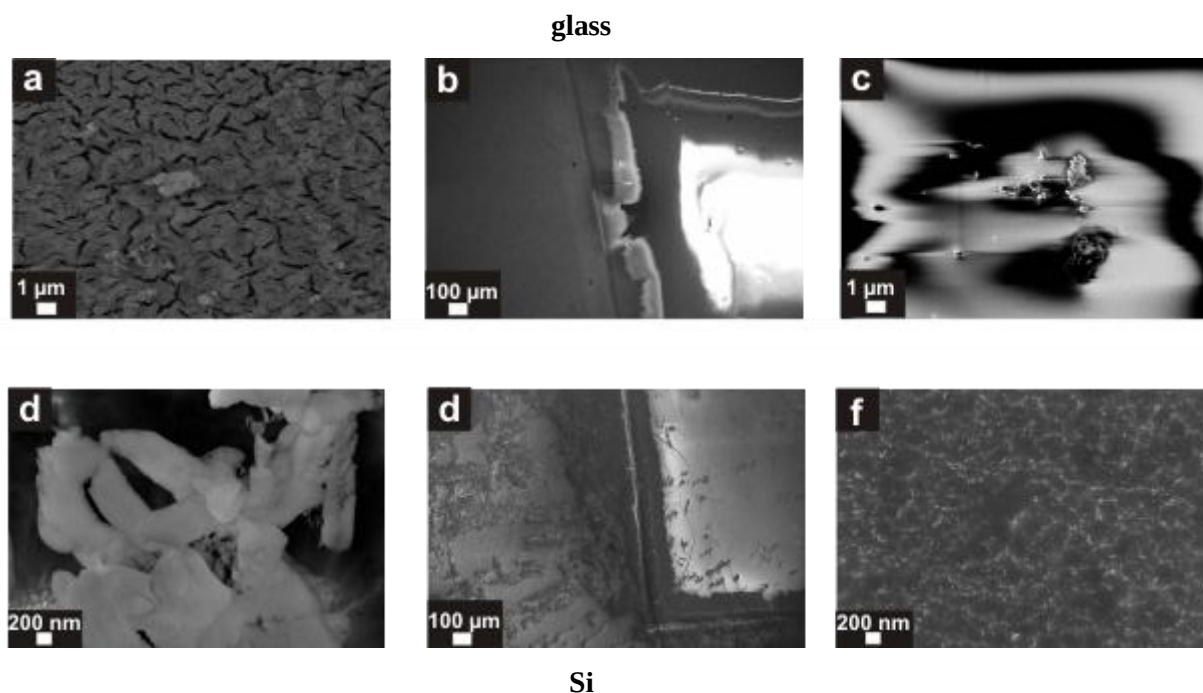


Fig. 5.6 Top-view SEM images of sample G for glass substrate (upper row) and Si substrate (bottom row). On the left is etched area, on the right is non-etched area and image in the middle is showing the interface between etched and non-etched areas.

In case of Si etching it was observed that using of CF_4 with small amount of Ar or O_2 (samples A and B) resulted in very slow etching rate because of polymer formation, while using of SF_6 increases the etching rate up to $1 \mu\text{m}/\text{min}$ (samples C-F). Increasing of power from 100 W to 500 W (sample G) improves the etching rate three times to $3,6 \mu\text{m}/\text{min}$. This observation is in great correlation with theory. For deep reactive ion etching of Si etching is widely used the so-called Bosch process invented by Laermer and Schilp [33] on inductively coupled plasma equipment. It is based on the periodic change of different gases for passivation (C_4F_8 or CF_4) and etching step (SF_6). In the deposition step the precursor gas (CHF_3 , CF_4 , C_2F_6 or higher molecular gas) is dissociated by the plasma. The ion and radical species undergo polymerization reactions. A passivating layer of nCF_2 is deposited in the etched patterns, on the sidewalls and on the mask. The deposited polymer film can be removed by ion bombardment with low energy. During the etching step the etching gas (for instance SF_6) is dissociated by the plasma, liberating high amounts of etching species. These species are necessary to remove the polymer film at the bottom of the pattern and to react with the silicon effectively [34].

The Bosch-process can be applied only in an ICP system (inductively coupled plasma) equipped with the corresponding software kit due to the short time switches between

deposition and etching and due to the high DC bias (high acceleration speed of ions to the substrate surface). We do not have the software kit in our ICP system for the Bosch process yet, therefore a CCP-RIE system was used for basic experiments with Si etching as well as with glass, MCD and NCD substrates.

In the case of glass substrates, the measured etching depths were very low (e.g. 80-90 nm after 20 min for samples A and B), or were even not measurable. This was caused by low power, short etching time and not appropriate mask material in these preliminary experiments. Relatively high etching depth was measured only for one sample (G) where high power was used (500 W) in SF_6/Ar gas chemistry using Si substrate as mask. In this case the etching rate was evaluated to 80-90 nm/min. Similar rate was achieved by Zeze et al. (92 nm/min) [35] in CF_4/Ar or CF_4/O_2 using thin metallic mask (Ni 150 nm). However, generally for glass etching mostly thick metal layers are used and ICP plasma systems because of hard glass material. A good summary of mask materials, etching chemistry and etching rates for deep reactive ion etching of glass substrates can be found in Ref. [36]. Based on that summary, the most used mask material is thick electroplated Ni film ($> 5 \mu\text{m}$) and etching chemistry of SF_6 gas (or combination of $\text{C}_4\text{F}_8/\text{O}_2$). In some cases, Cr can be used as etching material and gas chemistry of SF_6 combined with Ar [37]. Kolari [38] demonstrated using of thin AlN and Al_2O_3 as etching material of SiO_2 etching with high selectivity. A mixture of SF_6 and C_4F_8 was observed to etch SiO_2 with a rate of about 100 nm/min at 250 V bias (peak-to-peak) voltage, when Al_2O_3 and AlN had a zero etch rate.

These our preliminary results confirm that for deep reactive ion etching of Si and glass substrates it is necessary to solve the appropriate mask material and using of much powerful ICP plasma system.

5.4 Comparison of MCD and NCD films

Fig.5.7. shows the top-view and angle-view SEM images of non-etched MCD and NCD diamond films deposited with CO_2 or N_2 addition into CH_4/H_2 gas mixture, respectively. As we mentioned earlier, microcrystalline diamond film consists of large diamond crystals with size of 400-600 nm in diameter. Large crystals caused high roughness of the surfaces ($\sim 100\text{-}200 \text{ nm}$). In contrast to MCD, nanocrystalline diamond film has a smaller grain size (under 50 nm), and its surface morphology is more similar to diamond-like carbon (DLC) films with very low surface roughness ($\sim 50 \text{ nm}$).

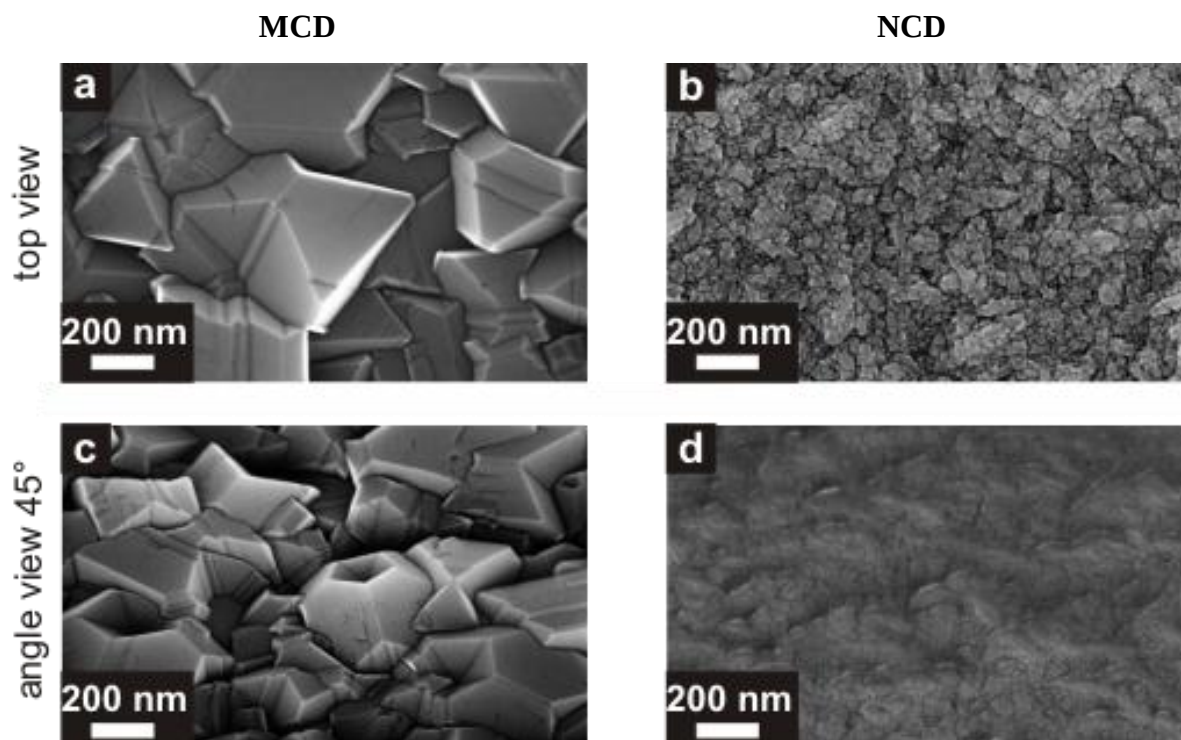


Fig. 5.7. SEM images of non-etched MCD and NCD diamond films.

For a comparison of the influence of different gas mixtures on etched micro- and nanocrystalline diamond surface, several samples were selected (see Tab. 5.2.). First, the influence of pure oxygen plasma, then the effect of CF_4 or SF_6 addition, and finally the combined effect of Ar and SF_6 gas mixture were studied.

Tab. 5.2. Selected samples for characterization and comparison of MCD and NCD etching (for other etching parameters see Tab. 4.3. and for etching rates Fig.5.12.).

Sample name	Gas mixture in sccm	Gas mixture in %
K	O_2 : 50	100% O_2
J	O_2/CF_4 : 48/2	4% CF_4 in O_2
L	SF_6/O_2 : 2/48	4% SF_6 in O_2
M	SF_6/Ar : 2/48	4% Ar in SF_6

a) Effect of pure oxygen plasma

The surface of MCD and NCD diamond films etched in pure oxygen plasma is shown in Fig. 5.8. The single diamond crystals, which were “damaged” by the process, can be clearly

distinguished in the top view images of the MCD film. Its surface topography was better shown on the angle view image, where small nanorods were observed. The surface of MCD film after etching was similar to NCD film after etching; both were characterized by small diamond nanorods close to each other. The only difference between them was related to the surface roughness (when studied over a large area) due to the high initial roughness of MCD films before the etching process (large diamond crystals).

It was apparent that etching by O_2 led to the formation of diamond needle-like structures (or so-called whiskers). The formation of these nanorods had multiple causes. The main cause was the vertical acceleration of ions to the substrate and physical sputtering also taking place besides chemical etching. Moreover, it is well-known that oxygen etches sp^2 carbon bonds much faster than sp^3 diamond bonds [39], which also resulted in the formation of needle-like structures along grain boundaries. Furthermore, these can also be formed within the grains at intrinsic defects in the crystals or in specific grains depending on their orientation [6]. In NCD films, the presence of more sp^2 carbon bonds at grain boundaries corresponded to an even more apparent formation of needle-like structures [13], [16].

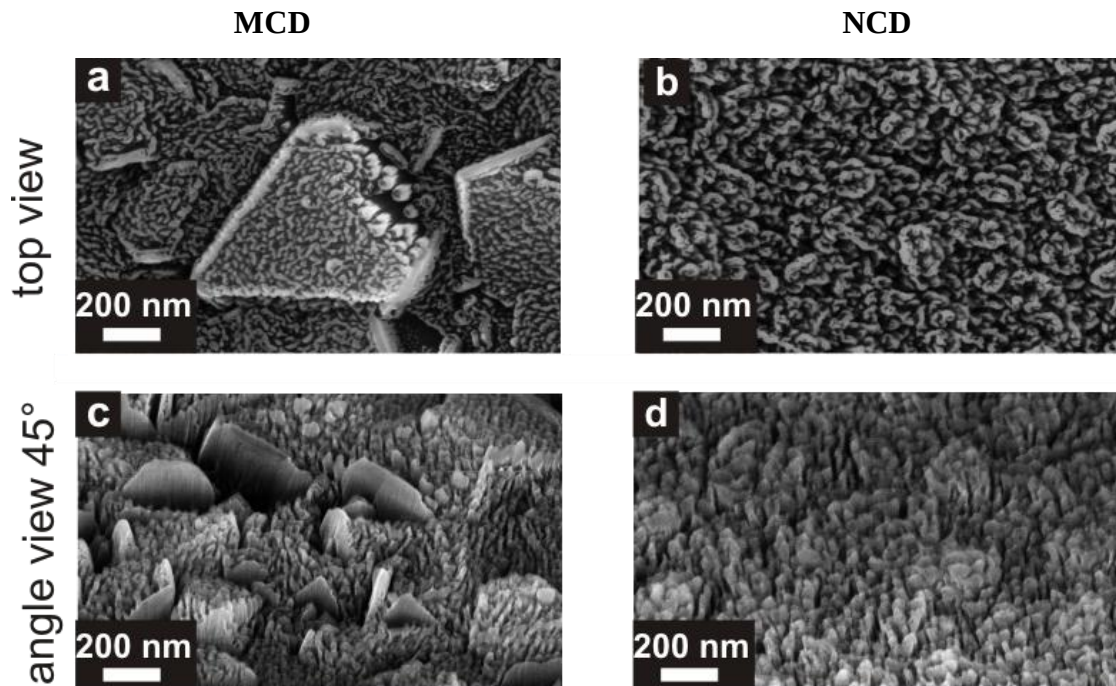


Fig. 5.8. Top-view SEM images of MCD (a) and NCD (b) films, and their angle-view by 45° (c and d, respectively) etched in pure oxygen plasma.

b) Effect of CF₄ additions to oxygen plasma

Even a small amount of CF₄ (4% CF₄ in O₂) has a strong influence on the surface morphology (see Fig.5.9.). In comparison to the previously etched sample in pure oxygen plasma, in this case the surface of MCD film is much flatter with sharp needles or walls at grain boundaries. A similar effect can also be observed on the top-view image of NCD film, however, in the case of NCD, it is not so well-marked. Formation of needles or thin walls at the edge of grains is due to defects and sp² carbon bonds, which have different etching rates than diamond bonds. Addition of CF₄ not only makes the surface flatter, but enhances the etching rate as well (see Fig. 5.12.). It is proposed that this is due to physical sputtering. The evidence of the enhanced effect of physical sputtering is the enhanced negative bias to -65 V (see Fig. 5.12.) [13].

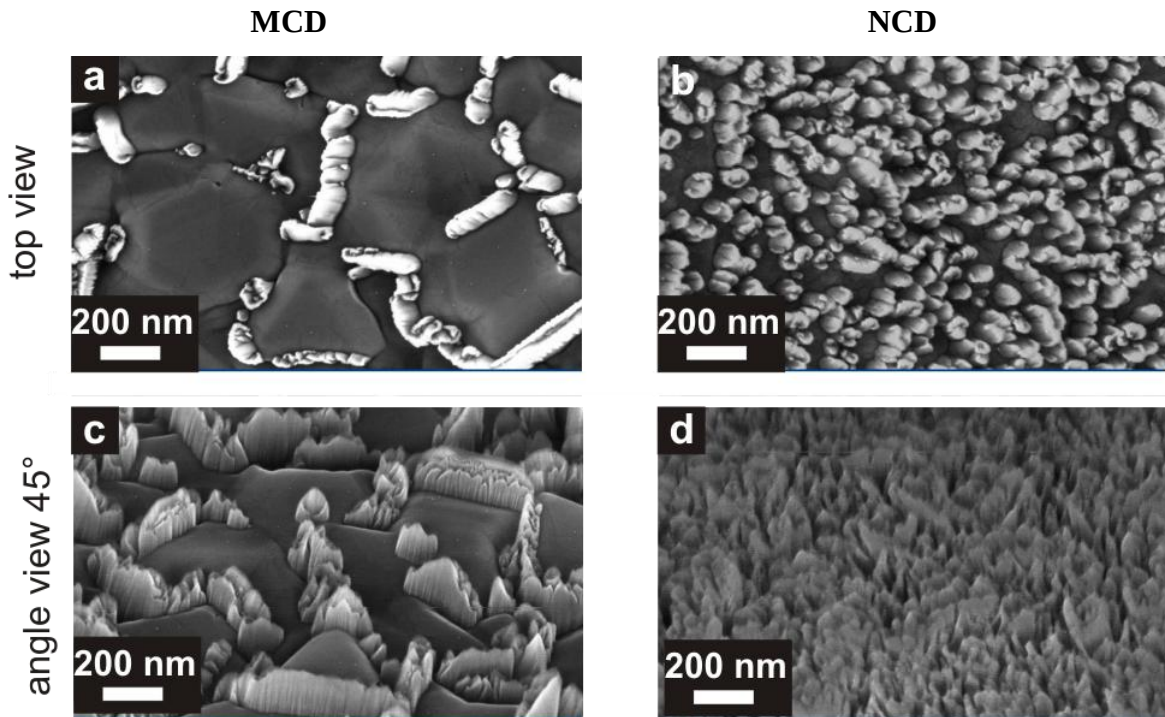


Fig. 5.9. Top-view SEM images of MCD (a) and NCD (b) films, and their angle-view by 45° (c and d, respectively) etched in CF₄/O₂ plasma.

c) Effect of SF₆ additions to oxygen plasma

The addition of a small amount of SF₆ (4%) into O₂ gas resulted in a similar surface morphology as in the case of pure oxygen plasma. The surface is roughened in the case of both MCD and NCD film, but with shorter nanorods. In addition, the etching rate was surprisingly decreased nearly twice in comparison to pure oxygen plasma or to CF₄/O₂ gas

chemistry (Fig. 5.12.). Previously studies and theoretical aspects predicted that addition of SF_6 has higher etching rate than with CF_4 because of S_xF_y is heavier molecule than CF_x , so the SF_6 bombardment effect is obviously higher than CF_4 . In addition, oxygen and sulfur hexafluoride (SF_6), when mixed together, create the oxyfluoride ion (OF^-). The oxyfluoride ion is also a powerful etching agent for diamond. The ion is particularly good at breaking the carbon-carbon molecular bonds of the diamond grain and removing the molecule quickly [40].

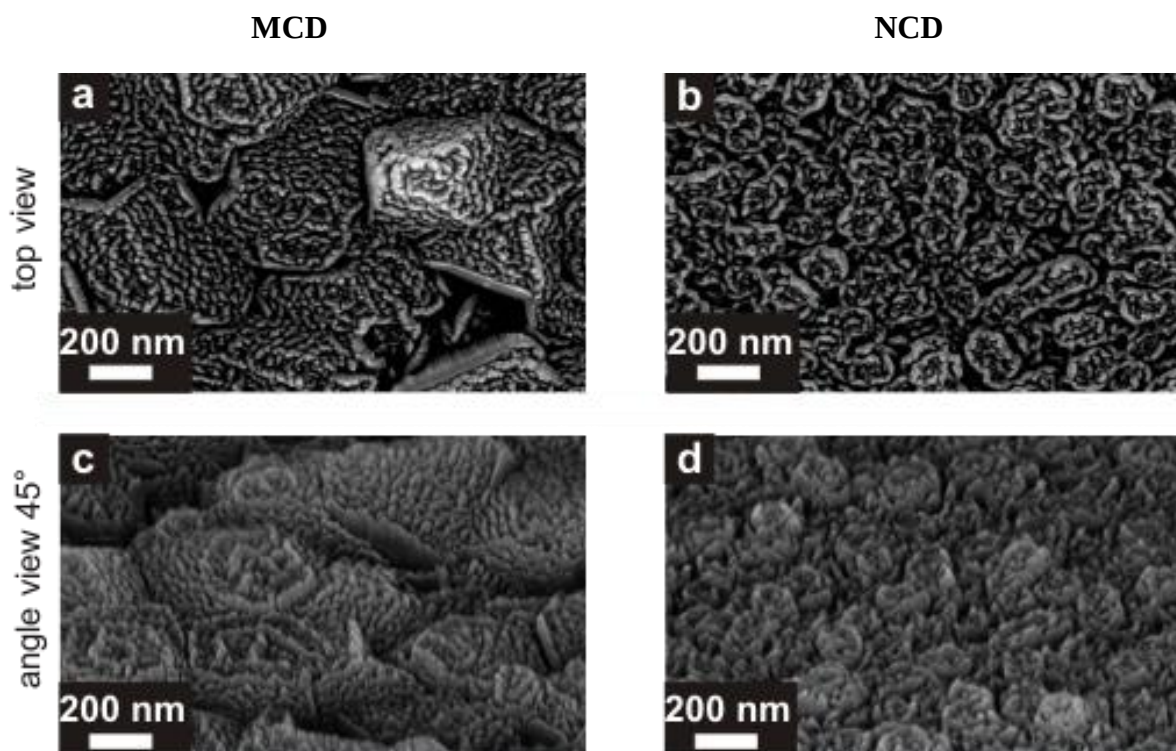


Fig. 5.10. Top-view SEM images of MCD (a) and NCD (b) films, and their angle-view by 45° (c and d, respectively) etched in SF_6/O_2 plasma.

It was already showed that using of very little or no SF_6 caused roughening of diamond during the etching due to a micro-masking effect. That is, small regions on the surface appear to be masked by impurities of some type that lead to spire-like (whisker) formation. This can lead to a significant increase in the surface roughness during the etching. In contrast, when sufficient SF_6 is added these micro-masking regions are minimized and the surface roughness did not significantly change [13], [41].

d) Effect of Ar additions to SF₆ plasma

Minimizing of micro-masking effect and high surface smoothness was achieved also by addition of 4% Ar into SF₆ gas (see Fig. 5.11.). The SEM images of samples show smooth surfaces without any nanorods or whiskers. In comparison to the previous samples, using Ar/SF₆ resulted in a lateral-like etching, where the diamond crystals are etched not only vertically from top to bottom, but also in a horizontal direction. The etching rate (20 nm/min) is comparable to pure oxygen and CF₄/O₂ plasma (26 nm/min and 28 nm/min, respectively).

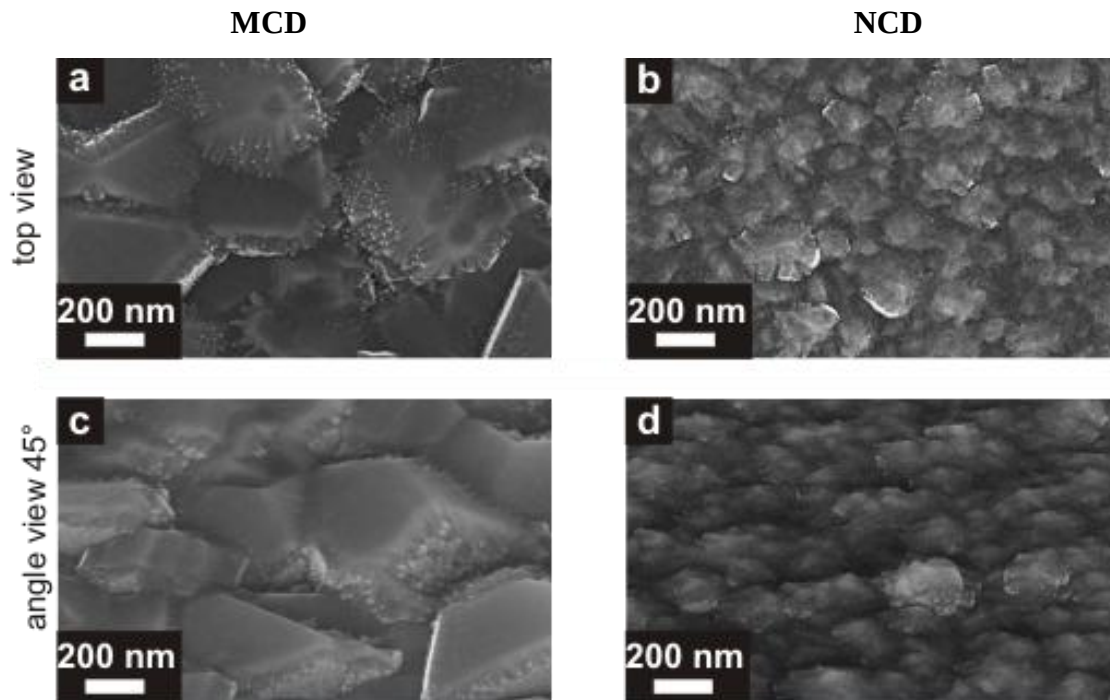


Fig. 5.11. Top-view SEM images of MCD (a) and NCD (b) films, and their angle-view by 45° (c and d, respectively) etched in SF₆/Ar plasma.

We showed that surface morphology of etched diamond films is strongly influenced by gas chemistry. Pure oxygen and small amount of SF₆ lead to formation of needle-like (or nanowhisker) structures. Substitution of O₂ by Ar resulted in smooth surface. This smoothing effect was demonstrated also by Tran et al. [42] who used combination of Ar/O₂/SF₆ in ratio of 6/28/2 sccm. It can be note, that using of not appropriate masking material can lead also to formation of nanowhiskers due to micro-masking effect as in the case of Si substrate. Good review of masking materials used at reactive ion etching of diamond films and their selectivity is summarized in Ref. [42]. Five mask materials were investigated for hard mask patterning of diamond: aluminium, gold, titanium, silicon nitride and silicon dioxide. It was shown that aluminium masks provided the highest selectivity ratio of diamond etch rate to

mask etch rate, both with and without SF₆ in the oxygen/argon feedgas. In addition, selectivity was not found to be dependent on mask feature size, and gold masks produced the least degree of micromasking. On other hand, it was published that for a Ti masking layer, addition of SF₆ causes the masking layer etch rate to increase and the diamond etch rate to decrease. Thus for Ti the selectivity is significantly reduced [13], [42].

Thus, it is clear that choosing an appropriate masking material and gas chemistry is an important step for deep reactive ion etching of diamond films with high aspect ratio.

Fig. 5.12. summarizes the etching rates for NCD films. For oxygen plasma the etching rate was 27 nm/min. After adding 4% CF₄ to the oxygen plasma, the etching rate increased to 29 nm/min. The lowest etching rate (13 nm/min) was found for the gas mixture of 4% SF₆ in oxygen. For the Ar/SF₆ gas mixture, the etching rate was 20 nm/min. For further insight into the etching process, the self-bias voltage induced during the etching process was also plotted (Fig. 5.12., orange). Self-bias voltage was –61 V for O₂ plasma, it achieved the highest value of –65 V for CF₄/O₂ plasma. For SF₆/O₂ and Ar/SF₆ plasma the self-bias voltage was –60 and –61 Volts, respectively.

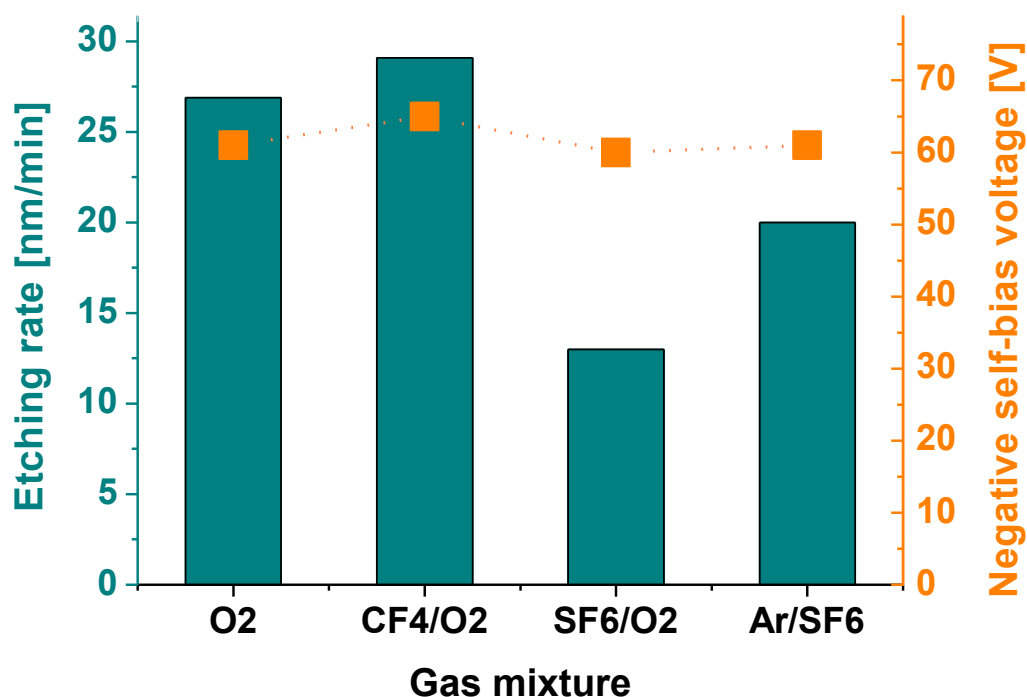


Fig. 5.12. Etching rate (columns on the left-side y-axis) and negative self-bias voltage (orange rectangles on the right-side y-axis) as the function of gas mixtures used for the etching of NCD films.

The formation of nanowhiskers is not a trivial process. It is often influenced by several sub-effects. First, sharp nanocones or nanowhiskers can be formed due to local inhomogeneities. These inhomogeneities are localized either along grain boundaries due to the differences in sp^2 vs. sp^3 carbon bonds or they are randomly spread within the grains due to intrinsic defects and impurities. The third kind of whiskers is regularly formed in specific grains which depend on crystallographic orientation [6].

For the MCD film, the primary diamond grains make a basic microscopic pattern. It is known that a higher concentration of sp^2 carbon atoms is preferentially localized at grain boundaries [43]. Taking into account the fact that oxygen etches sp^2 carbon bonds much faster than sp^3 carbon bonds, the grains become microscopically visible due to the edges. Similar selectivity in etching of sp^2/sp^3 bonds was observed for atomic hydrogen [44].

The decrease of whisker features when CF_4 is added to O_2 plasma can be attributed to the lateral etching of diamond by CF_4 gas mixtures. Adding even a small amount of CF_4 was found to smooth (polish) the diamond surface [6], [19]. Furthermore, CF_4 makes the diamond surface not only flatter but also increases the etching rate [45]. This is in good agreement with our observation when the etching rate slightly increased from 27 nm/min for the oxygen to 29 nm/min for the CF_4/O_2 gas mixture (Fig.5.12.). Combining effects of faster etching and flattening, the individual grains should be homogeneously etched within their whole surface except at grain boundaries. As mentioned above, higher density of sp^2 carbon bonds and defects is assumed at grain boundaries. Thus, these “non-diamond” phases can disturb the lateral etching at grain boundaries, i.e. they are differently etched than diamond bonds.

However, controversial results were observed for the addition of 4% SF_6 to the O_2 gas. First, the etching rate was the lowest (13 nm/min). This observation is a little bit confusing because a more intensive lateral-like etching effect was expected. In a previous study it was shown that adding SF_6 to the Ar/O_2 gas mixture resulted in a flattening of diamond films etched by ECR plasma [42]. Previous experimental work and theoretical studies predicted that the addition of SF_6 should enhance the etching rate in comparison to the CF_4 gas mixture. This prediction is based on the fact that S_xF_y is a heavier molecule than CF_x , so the SF_6 bombardment effect should obviously be higher than the CF_4 one. Moreover, when oxygen and sulfur hexafluoride (SF_6) are mixed together, oxyfluoride ions (OF^-) are formed which further enhanced (accelerated) the diamond etching [40]. However, this prediction is valid only in some cases. The masking material used was found to be an important parameter which influenced the etching rate of diamond. Using SiO_2 and Si_3N_4 masks resulted in an increased etching rate after the addition of SF_6 to the O_2 gas [42]. Compared to this observation, the

etching rate was 2-4 times lower for Al, Ti and Au masks. The main origin of these differences is not clear but the authors proposed that the co-deposition of nonvolatile compounds on the diamond surface in the latter case might be involved. Presently we do not know why the etching rate falls down in our case. One noticeable difference in this study is the fact that we used capacitively coupled plasma while the former study used ECR plasma.

Finally, the addition of Ar (4%) to SF₆ resulted in surface flattening. For Ar plasmas it is well known that the etching process is enhanced by physical etching (i.e. sputtering) due to surface bombardment by heavy argon ions. Similar observations were reported for diamond etching in H₂/Ar plasma [16], [39]. In this case, the diamond etching consisted of physical and chemical processes. The physical process involved sputtering and graphitization of the top diamond layer by energetic ions. For this process, ion energy and ion species are the dominant process factors. The chemical process was based on the preferential etching of graphitized or amorphous carbon by reactive hydrogen atoms/ions [16]. Depending on the primary structure of diamond film, the process can have a tendency to form conical/whisker structures which have to correlate with the original film structure [46]. It can be assumed that this tendency is significantly influenced or even disturbed by argon bombardment. As the surface nano-features are formed the incoming Ar ions can very effectively graphitize these nano-features which are suddenly and preferentially removed by the chemical process. Thus, the diamond film is flattened due to the suppression of the perpendicular etching that was observed for O₂ or CF₄/O₂ plasmas [13].

5.5 Diamond nanostructures with enhanced aspect ratio

In this section it is described the fabrication method of high aspect ratio rod-like diamond nanostructures. For experiments MCD diamond films were used, which were deposited by the following parameters: MW power: 2500 W, total gas pressure: 5000 Pa, 1 % of methane diluted in hydrogen, temperature: 700°C, growth time: 4 h. Thickness of diamond layer was evaluated to ~1.6 µm with crystal size up to 500 nm. The morphology of MCD film is shown on Fig. 5.13. As mask material nano-sized gold droplets were used. Their preparation is described above (see Fig. 4.1).

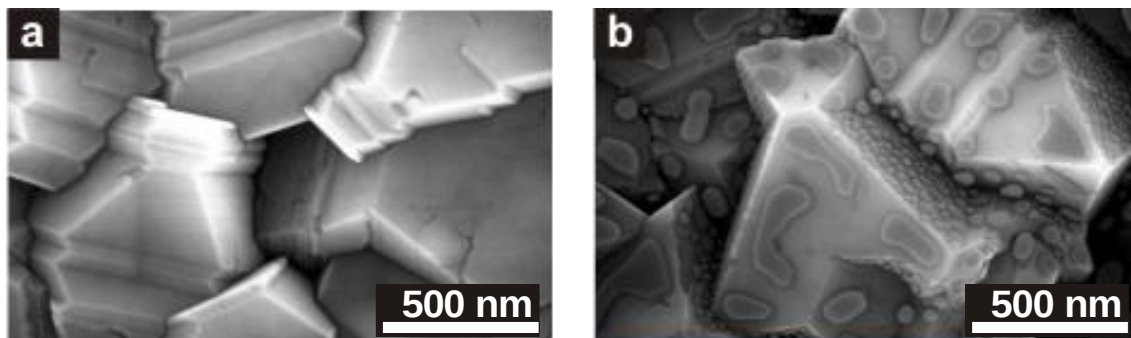


Fig.5.13. SEM images of diamond surface before etching without mask (a) and with mask (b).

Etching conditions were chosen based on the previous results. In first objective, pure O_2 and small amount of CF_4 gas in O_2 (4%) gas mixture was studied. The other etching conditions were kept at constant values: RF power 100 W, pressure 12 Pa and etching time 10 min. Two different masks were used labelled as “small” and “large” mask. Small mask consisted of gold droplets of ~ 10 -30 nm in diameters, and big mask has gold droplets of 150-250 nm in diameter. Gold droplets on MCD film for big mask are shown on Fig.5.13b.

Figure 5.14. shows the morphology of diamond films after etching. Due to gold nano-droplets mask the surface was changed to needle-like for small mask, and diamond nanorods for big mask. After 10 min of etching time in pure oxygen, the length of the nanorods was evaluated to 250 nm (see Fig. 5.14c). In the case of 4% of CF_4 in O_2 plasma (small mask, Fig.5.14b) the gold nano-droplets mask was partially etched away and the nanorods were almost destroyed in comparison to pure oxygen plasma etching.

Beside these experiments, other experimental sets were done, where the ratio of CF_4 to O_2 was studied, as well as the effect of increased RF power. Some results of these experiments are shown in Fig. 5.15. This figure shows the cross-section SEM images of etched diamond nanorods by pure O_2 and by 60% of CF_4 in O_2 gas mixture at 300 W of RF power using “big mask” of gold droplets. As we can see, by etching of MCD film for 10 min was nearly reached the silicon substrate surface (Fig. 5.15a). Beside larger diamond nanorods in diameter, also smaller nanotips are observed. These nanotips formed due to sp^2 carbon bonds at grain boundaries and due to defects present in diamond crystals. Addition of CF_4 into the gas mixture inhibited the formation of such nanotips, but simultaneously it damaged the gold droplets used as masking material, and hence it lead to worse result.

After optimization we found that good conditions for nanorods fabrication using CCP-RIE system are low RF power (<150 W), low pressure (12 Pa) and using of CF₄/O₂ gas chemistry. The formation of high aspect ratio (1:6) nanorods was achieved.

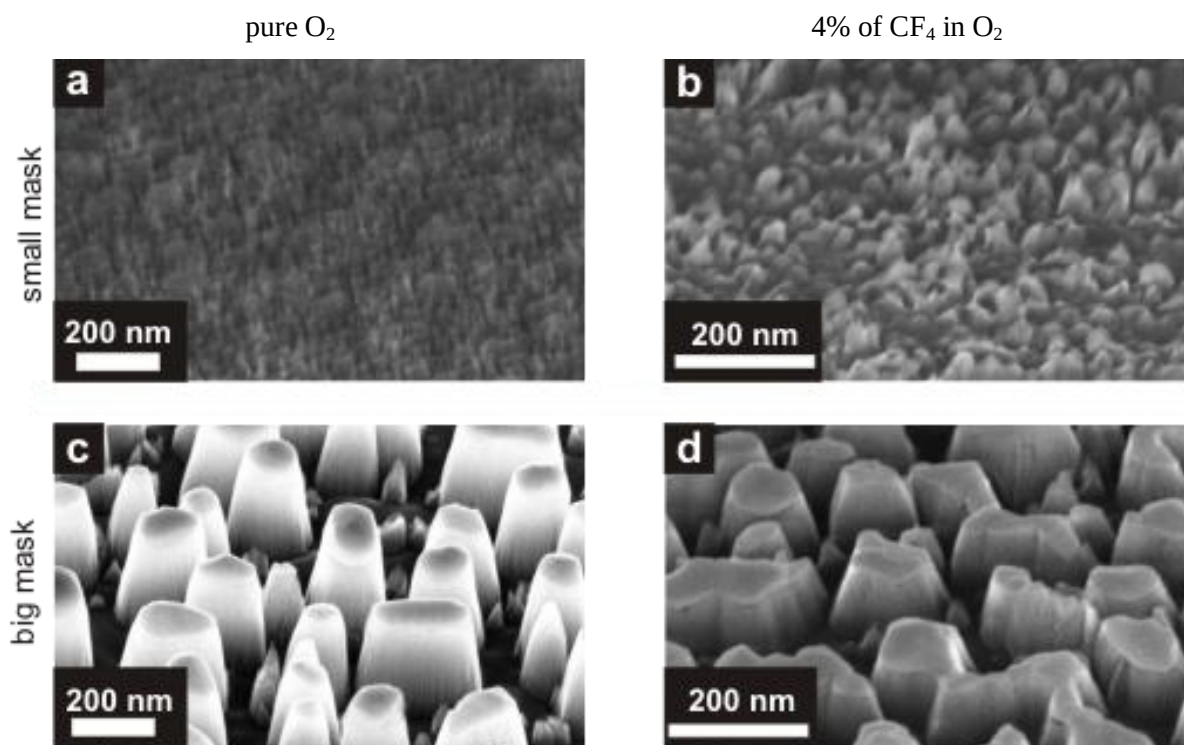


Fig.5.14. SEM images of diamond nanorods etched in different plasma for different mask labelled as “small” (upper row) and “big” mask (bottom row). On the left: pure oxygen plasma, on the right 4% of CH₄ in O₂.

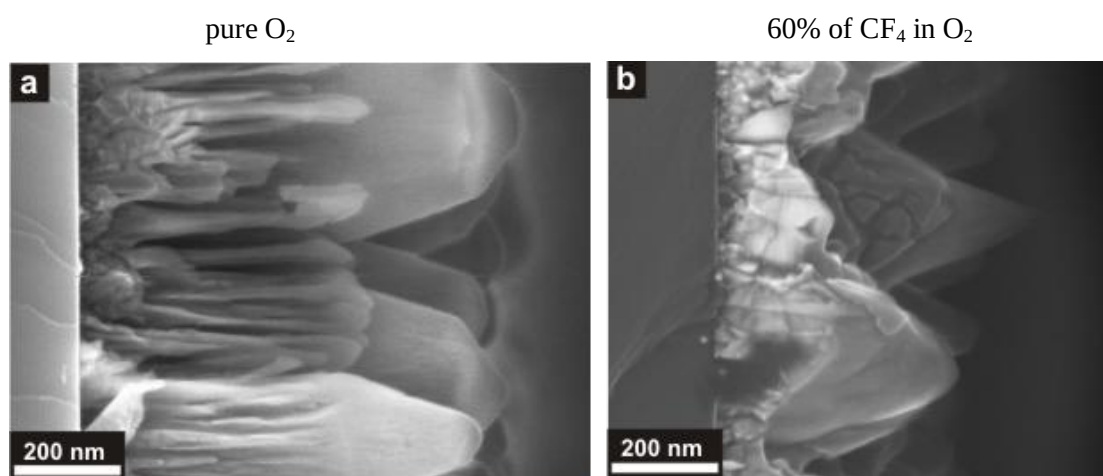


Fig. 5.15. SEM images of cross-section view of diamond nanorods (etching parameters: RF power: 300 W, pressure 12 Pa and etching time 10 min).

Conclusion

This work reviewed structuring of diamond films. The nanostructuring of diamond films by reactive ion etching was also experimentally studied. Morphological properties of microcrystalline (MCD) and nanocrystalline diamond (NCD) films were compared and studied. The structuring of diamond films was done using various gas mixtures (CF_4 , O_2 , SF_6 and Ar) in capacitively coupled RF plasma. Etching conditions were optimized for high etching rate, good enough selectivity and achieving wished surface morphology. As the second objective, silicon and glass substrates were structured (etched) before the diamond deposition. This strategy allows a direct fabrication of photonic and optical elements. The morphology of etched samples was characterized by Scanning Electron Microscopy and Atomic Force Microscopy. The etching rates and depth profiles were evaluated using optical and profilometric measurements.

First, the state of the art of diamond film structuring by reactive ion dry etching was described (top-down strategy), as well as the current status of direct (selective) growth of diamond films from seeding layer (bottom-up).

Diamond films were prepared using a focused microwave plasma chemical vapour deposition system by addition of CO_2 (for MCD) or N_2 (for NCD) into the CF_4/H_2 gas mixture. For etching, several mask materials were used: evaporated continuous metal films - Ni, Au, Ti/Ni; self-assembled metal nanoparticles - Au, Ni, Al; simple mechanical mask - piece of Si wafer and without any mask. We observed that the etching mask (primary thin continuous film of Au, or Ti/Ni layer) was in some cases partially or entirely destroyed after etching. This means the mask material used for etching must be carefully selected based on the etching conditions (high ion or electron bombardment). A good choice seemed to be electroplated Ni film with a thickness of up to a few micrometers.

In the case of Si etching, it was observed that using CF_4 with a small amount of Ar or O_2 resulted in very low etching rate because of polymer formation, while using SF_6 increased the etching rate up to $1\text{ }\mu\text{m}/\text{min}$. Increasing the power from 100 W to 500 W improves the etching rate three times to $3.6\text{ }\mu\text{m}/\text{min}$. This observation is in great correlation with theory.

In the case of glass substrate, relatively high etching depth was measured only for one sample, where high power was used (500 W) in SF_6/Ar gas chemistry. The etching rate was evaluated as 80-90 nm/min. Our preliminary results showed that for deep reactive ion etching

of Si and glass substrates, it is necessary to choose an appropriate mask material, and to use a much more powerful ICP plasma system.

In the case of MCD and NCD etching, we observed that the etching by O_2 plasma led to the formation of diamond needle-like structures (or so-called whiskers). Generally, we can claim that the addition of CF_4 made the surface flatter and enhanced the etching rate. The addition of a small amount of SF_6 (4%) into O_2 gas resulted in a similar surface morphology as in the case of pure oxygen plasma. The surface was roughened in the case of both MCD and NCD film, but with shorter nanorods. In addition, the etching rate was surprisingly decreased nearly twice in comparison to pure oxygen plasma. Moreover, using very little or no SF_6 caused roughening of diamond during the etching due to a micro-masking effect. That is, small regions on the surface appear to be masked by impurities of some type that lead to spire-like (whisker) formation. This can lead to a significant increase in the surface roughness during the etching. In contrast, when sufficient SF_6 was added these micro-masking regions were minimized. Minimizing the micro-masking effect and high surface smoothness was also achieved by the addition of 4% Ar into SF_6 gas. Ar/ SF_6 resulted in a lateral-like etching, where the diamond crystals were etched not only vertically from top to bottom, but also in a horizontal direction. The etching rate (20 nm/min) was comparable to pure oxygen and CF_4/O_2 plasma (26 nm/min and 28 nm/min, respectively).

Obtained results from MCD and NCD etching were used for producing of a diamond nanorod array with a high aspect ratio. These diamond nanostructures have needle-like structures of several nm in diameter, as well as larger diamond nanorods of 150-250 nm in diameter. Such nanostructures could find many applications in electronics and optics (field emission devices, AFM tips, photonic crystals), sensorics (gas sensors, biosensors), as well as in tissue engineering.

The next step in the fabrication of diamond nanorods with high aspect ratio will be the utilization of a more powerful ICP plasma system

References

- [1] F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, “Man-Made Diamonds,” *Nature*, vol. 176, pp. 51–54, 1955.
- [2] P. W. May, “Diamond thin films: a 21st-century material,” *Philos. Trans. R. Soc. Lond. Ser. Math. Phys. Eng. Sci.*, vol. 358, no. 1766, pp. 473–495, Jan. 2000.
- [3] S. Koizumi, C. E. Nebel, M. Nesladek, and Wiley InterScience (Online service), *Physics and applications of CVD diamond*. Weinheim: Wiley-VCH, 2008.
- [4] M. Kalbacova, L. Michalikova, V. Baresova, A. Kromka, B. Rezek, and S. Kmoch, “Adhesion of osteoblasts on chemically patterned nanocrystalline diamonds,” *Phys. Status Solidi B*, vol. 245, no. 10, pp. 2124–2127, 2008.
- [5] E. Verveniatis, J. Čermák, A. Kromka, M. Ledinský, Z. Remeš, and B. Rezek, “Local electrostatic charging differences of sub-100 nm nanocrystalline diamond films,” *Phys. Status Solidi A*, vol. 207, no. 9, pp. 2040–2044, 2010.
- [6] H. Uetsuka, T. Yamada, and S. Shikata, “ICP etching of polycrystalline diamonds: Fabrication of diamond nanotips for AFM cantilevers,” *Diam. Relat. Mater.*, vol. 17, no. 4–5, pp. 728–731, Apr. 2008.
- [7] O. Babchenko, A. Kromka, K. Hruska, M. Michalka, J. Potmesil, and M. Vanecek, “Nanostructuring of diamond films using self-assembled nanoparticles,” *Cent. Eur. J. Phys.*, vol. 7, no. 2, pp. 310–314, Mar. 2009.
- [8] M. Kalbacova, A. Broz, O. Babchenko, and A. Kromka, “Study on cellular adhesion of human osteoblasts on nanostructured diamond films,” *Phys. Status Solidi B*, vol. 246, no. 11–12, pp. 2774–2777, 2009.

- [9] O. Babchenko, A. Kromka, K. Hruska, M. Kalbacova, A. Broz, and M. Vanecek, "Fabrication of nano-structured diamond films for SAOS-2 cell cultivation," *Phys. Status Solidi A*, vol. 206, no. 9, pp. 2033–2037, 2009.
- [10] N. Yang, H. Uetsuka, E. Osawa, and C. E. Nebel, "Vertically Aligned Diamond Nanowires for DNA Sensing," *Angew. Chem. Int. Ed.*, vol. 47, no. 28, pp. 5183–5185, 2008.
- [11] M. Davydova, A. Kromka, B. Rezek, O. Babchenko, M. Stuchlik, and K. Hruska, "Fabrication of diamond nanorods for gas sensing applications," *Appl. Surf. Sci.*, vol. 256, no. 18, pp. 5602–5605, Jul. 2010.
- [12] Q. Wang, S. L. Qu, S. Y. Fu, W. J. Liu, J. J. Li, and C. Z. Gu, "Chemical gases sensing properties of diamond nanocone arrays formed by plasma etching," *J. Appl. Phys.*, vol. 102, no. 10, p. 103714, Nov. 2007.
- [13] M. Domonkos, T. Izak, O. Babchenko, M. Varga, K. Hruska, and A. Kromka, "Mask-Free Surface Structuring of Micro- and Nanocrystalline Diamond Films by Reactive Ion Plasma Etching," *Adv. Sci. Eng. Med.*, vol. 6, no. 7, pp. 780–784, Jul. 2014.
- [14] L. Meng, J. Zhang, and X. D. Zhu, "Carbon cone arrays by double-bias assisted hot filament plasma chemical vapor deposition," *Thin Solid Films*, vol. 516, no. 10, pp. 2981–2986, Mar. 2008.
- [15] T. Izak, "Using of selfassembled gold nano-sized droplets for fabrication of vertically aligned diamond nanorods," presented at the 20th Joint Seminar Development of Materials Science in Research and Education, Bořetice, 2010.
- [16] Y. S. Zou, Y. Yang, W. J. Zhang, Y. M. Chong, B. He, I. Bello, and S. T. Lee, "Fabrication of diamond nanopillars

- and their arrays,” *Appl. Phys. Lett.*, vol. 92, no. 5, p. 053105, Feb. 2008.
- [17] M. Kalbacova, B. Rezek, V. Baresova, C. Wolf-Brandstetter, and A. Kromka, “Nanoscale topography of nanocrystalline diamonds promotes differentiation of osteoblasts,” *Acta Biomater.*, vol. 5, no. 8, pp. 3076–3085, Oct. 2009.
- [18] C. L. Lee, H. W. Choi, E. Gu, M. D. Dawson, and H. Murphy, “Fabrication and characterization of diamond micro-optics,” *Diam. Relat. Mater.*, vol. 15, no. 4–8, pp. 725–728, Apr. 2006.
- [19] H. Gamo, K. Shimada, M. Nishitani-Gamo, and T. Ando, “Ultrafine Patterning of Nanocrystalline Diamond Films Grown by Microwave Plasma-Assisted Chemical Vapor Deposition,” *Jpn. J. Appl. Phys.*, vol. 46, no. 9B, pp. 6267–6271, 2007.
- [20] S. Potocký, “Diamond structures grown from polymer composite nanofibers,” presented at the 22nd Joint Seminar Development of Materials Science in Research and Education, Lednice Czech Republic, 2012.
- [21] A. Biswas, I. S. Bayer, A. S. Biris, T. Wang, E. Dervishi, and F. Faupel, “Advances in top-down and bottom-up surface nanofabrication: techniques, applications & future prospects,” *Adv. Colloid Interface Sci.*, vol. 170, no. 1–2, pp. 2–27, Jan. 2012.
- [22] O. Babchenko, T. Izak, E. Ukraintsev, K. Hruska, B. Rezek, and A. Kromka, “Toward surface-friendly treatment of seeding layer and selected-area diamond growth,” *Phys. Status Solidi B*, vol. 247, no. 11–12, pp. 3026–3029, 2010.
- [23] A. V. Sumant, P. U. P. A. Gilbert, D. S. Grierson, A. R. Konicek, M. Abrecht, J. E. Butler, T. Feygelson, S. S. Rotter, and R. W. Carpick, “Surface composition, bonding,

- and morphology in the nucleation and growth of ultra-thin, high quality nanocrystalline diamond films,” *Diam. Relat. Mater.*, vol. 16, no. 4–7, pp. 718–724, Apr. 2007.
- [24] A. Kromka, O. Babchenko, H. Kozak, K. Hruska, B. Rezek, M. Ledinsky, J. Potmesil, M. Michalka, and M. Vanecek, “Seeding of polymer substrates for nanocrystalline diamond film growth,” *Diam. Relat. Mater.*, vol. 18, no. 5–8, pp. 734–739, May 2009.
- [25] Š. Potocký, T. Ižák, B. Rezek, P. Tesárek, and A. Kromka, “Transformation of polymer composite nanofibers to diamond fibers and films by microwave plasma-enhanced CVD process,” *Appl. Surf. Sci.*, vol. 312, pp. 188–191, Sep. 2014.
- [26] Verdonck Patrick, “Oficina de Micro- fabricação: Projeto e Construção de CI’s MOS.” São Paulo, Brazil, 2006.
- [27] D. M. Manos and D. L. Flamm, *Plasma etching: an introduction*. Boston: Academic Press, 1989.
- [28] H. Jansen, H. Gardeniers, M. de Boer, M. Elwenspoek, and J. Fluitman, “A survey on the reactive ion etching of silicon in microtechnology,” *J. Micromechanics Microengineering*, vol. 6, no. 1, p. 14, 1996.
- [29] T. Ižák, “Investigation of nucleation and growth of diamond and DLC thin films.” PhD Thesis, Slovak University of Technology in Bratislava, 2011.
- [30] [Online]. Available:
http://www.oxfordplasma.de/technols/icp_ecr.htm.
 [Accessed: 13-Dec-2013].
- [31] J. C. Arnault, L. Demuynck, C. Speisser, and F. Le Normand, “Mechanisms of CVD diamond nucleation and growth on mechanically scratched Si(100) surfaces,” *Eur. Phys. J. B*, vol. 11, no. 2, pp. 327–343, Sep. 1999.

- [32] Z. Remes, A. Kromka, and M. Vanecek, "Towards optical-quality nanocrystalline diamond with reduced non-diamond content," *Phys. Status Solidi A*, vol. 206, no. 9, pp. 2004–2008, Sep. 2009.
- [33] F. Laermer and A. Schilp, "Method of anisotropically etching silicon," 5501893, 26-Mar-1996.
- [34] K. Richter, M. Orfert, S. Howitz, and S. Thierbach, "Deep plasma silicon etch for microfluidic applications," *Surf. Coat. Technol.*, vol. 116, pp. 461–467, Sep. 1999.
- [35] D. A. Zeze, R. D. Forrest, J. D. Carey, D. C. Cox, I. D. Robertson, B. L. Weiss, and S. R. P. Silva, "Reactive ion etching of quartz and Pyrex for microelectronic applications," *J. Appl. Phys.*, vol. 92, no. 7, pp. 3624–3629, Oct. 2002.
- [36] S. Queste, R. Salut, J.-Y. Rauch, and C. G. K. Malek, "Manufacture of microfluidic glass chips by deep plasma etching, femtosecond laser ablation, and anodic bonding," *Microsyst. Technol.-Micro- Nanosyst.-Inf. Storage Process. Syst.*, vol. 16, no. 8–9, pp. 1485–1493, Aug. 2010.
- [37] T. Ichiki, Y. Sugiyama, T. Ujiie, and Y. Horiike, "Deep dry etching of borosilicate glass using fluorine-based high-density plasmas for micrbelectromechanical system fabrication," *J. Vac. Sci. Technol. B*, vol. 21, no. 5, pp. 2188–2192, Oct. 2003.
- [38] K. Kolari, "High etch selectivity for plasma etching SiO₂ with AlN and Al₂O₃ masks," *Microelectron. Eng.*, vol. 85, no. 5–6, pp. 985–987, Jun. 2008.
- [39] Q. Wang, C. Z. Gu, Z. Xu, J. J. Li, Z. L. Wang, X. D. Bai, and Z. Cui, "Diamond cone arrays with controlled morphologies formed by self-organized selective ions sputtering," *J. Appl. Phys.*, vol. 100, no. 3, p. 034312, Aug. 2006.

- [40] C. L. Chao, W. C. Chou, K. J. Ma, T. T. Chen, Y. M. Liu, S. W. Huang, and H. Y. Lin, "Machining of CVD diamond film by RIE, Laser Ablation and Thermo-chemical Polishing(Ultra-precision machining)," *Proc. Int. Conf. Lead. Edge Manuf. 21st Century LEM21*, vol. 2005, no. 3, pp. 1063–1068, Oct. 2005.
- [41] D. T. Tran, T. A. Grotjohn, D. K. Reinhard, and J. Asmussen, "Microwave plasma-assisted etching of diamond," *Diam. Relat. Mater.*, vol. 17, no. 4–5, pp. 717–721, Apr. 2008.
- [42] D. T. Tran, C. Fansler, T. A. Grotjohn, D. K. Reinhard, and J. Asmussen, "Investigation of mask selectivities and diamond etching using microwave plasma-assisted etching," *Diam. Relat. Mater.*, vol. 19, no. 7–9, pp. 778–782, Jul. 2010.
- [43] Q. Yang, W. Chen, C. Xiao, A. Hirose, and R. Sammynaiken, "Simultaneous growth of well-aligned diamond and graphitic carbon nanostructures through graphite etching," *Diam. Relat. Mater.*, vol. 14, no. 10, pp. 1683–1687, Oct. 2005.
- [44] "H.O.Pierson - Handbook of Carbon, Graphite, Diamond and Fullerenes," *Scribd*. [Online]. Available: <http://www.scribd.com/doc/8968836/HOPierson-Handbook-of-Carbon-Graphite-Diamond-and-Fullerenes>. [Accessed: 28-Nov-2013].
- [45] T. Izak, A. Kromka, O. Babchenko, M. Ledinsky, K. Hruska, and E. Verveniots, "Comparative study on dry etching of polycrystalline diamond thin films," *Vacuum*, vol. 86, no. 6, pp. 799–802, Jan. 2012.
- [46] Y. S. Zou, K. L. Ma, W. J. Zhang, Q. Ye, Z. Q. Yao, Y. M. Chong, and S. T. Lee, "Fabrication of diamond nanocones and nanowhiskers by bias-assisted plasma

etching,” *Diam. Relat. Mater.*, vol. 16, no. 4–7, pp. 1208–1212, Apr. 2007.