1 Introduction Nanocrystalline diamond (NCD) film, due to its extraordinary properties, is a perspective material for wide range of applications. Adequately, developing of a suitable structuring technique is needed for realization of any device [1, 2]. However, diamond chemical inertness and mechanical hardness make conventional structuring methods less favorable. A direct growth of diamond structures represents alternative solution. The direct growth, also known as selected-area deposition (SAD), is mostly realized by applying the treatment of seeding (i.e., nucleation) layer before the diamond growth [1, 2].

The SAD growth of diamond structures has been achieved by several treatment techniques. One of the mostly used techniques is removal of diamond nuclei (seeds) from defined areas [3, 4]. Another treatment is based on bias-enhanced diamond nucleation process on pre-defined areas using SiN or Pt coatings [5, 6]. The direct “printing” of diamond seeds on the selected area by ink-jet printing has been shown as the alternative technique too [7]. Also wet chemical etching of SiO\textsubscript{2} on selected areas by buffer oxide etchant resulted in the SAD growth [8]. However, common limitations of the above mentioned treatments are either aggressive wet chemistries or specific type of substrate material.

In this paper we present a technological approach suitable for SAD growth with minimal damage of the substrate surface. A lithographic treatment of sandwich structure polymer/seeding layer/polymer followed by reactive ion etching is shown as the optimal treatment technique for patterned diamond growth. Selectivity and quality of such diamond structures are characterized by scanning electron microscopy, Raman spectroscopy, and atomic force microscopy.

2 Experimental details As substrates, polished Si (100) 550 \micron thick wafers with 1.5 \micron LTO silicon dioxide layer (On Semiconductors, Czech Republic) were used. Three sets of samples were prepared implementing: (A) reactive ion etching through photolithographical mask, (B) photolithographical processing with two polymer layers, and (C) combination of the A and B strategies.

In the strategy A, Si/SiO\textsubscript{2} substrates were seeded with diamond nanoparticles by ultrasonic agitation in a diamond suspension (diamond powder NanoAmando, New Metals and Chemicals Corp. Ltd., Kyobashi). Obtained typical seeds density was in range up to \(10^{11} \text{cm}^{-2}\) [9]. Next, the samples were covered with a positive photoresist (OFPR polymer) by using a spin-coating. The polymer drying
temperature was 100°C. Optical photolithography (UV irradiation through the shadow mask and developing in the solvent) was used for photore sist processing. In this way, polymer structures with stripes and gaps 100 μm wide were prepared. After then, it followed the dry etching process which removed seeds from areas not protected by polymer. Dry etching was provided by CF4/O2 rf plasma maintained at 100 W under pressure of 150 mTorr (Phantom LT, Trion Technology). The duration of etching process was 5 min. A schematic illustration of strategy A is shown in Fig. 1 – Set A.

In the strategy B, Si/SiO2 wafers were first covered by spin-coating with OFPR layer as show Fig. 1 – Set B, and dried at 100°C. Then they were seeded with diamond nanoparticles by ultrasound agitation (the same technique which was used for samples in the Set A). The seeding layer was covered by OFPR layer and dried. In this way, diamond seeds are packed between two photosensitive layers. Such sandwich-like structure results in patterned structures prepared only by an optical lithography.

In the strategy C (Fig. 1 – Set C), Si/SiO2 wafers were first processed as in the strategy B. Then, the reactive ion etching for 3 min (plasma parameters were the same as in the strategy A) was used as the final treatment step.

Subsequently, growth of NCD thin films on all pre-treated samples was performed in a microwave plasma CVD system (AIXTRON P6) from a methane/hydrogen gas mixture. Process parameters were as follows: microwave power 2.5 kW, 1% methane in hydrogen, total gas pressure 50 mbar, substrate temperature 800°C, and total growth time 3 h.

Surface morphology of the grown samples was investigated by scanning electron microscope e_LiNE system (Raith). Digital SEM images were processed by the software Atlas (Tescan Ltd, Czech Republic) to calculate the densities of diamond crystals in unwanted areas. Diamond character of the grown structures was confirmed by Raman spectroscopy (Renishaw inVia Reflex Raman microscope using the excitation wavelength of 325 nm and 40x objective).

3 Results and discussion SEM images of the diamond structures grown after the treatment strategies A, B, and C are shown in Fig. 2. A clear difference between areas with intended (on-stripe) and unintended (off-stripe) diamond growth is observed for all samples. A fully closed layer is observed on the intended areas.

The surface morphology of sample A, i.e., where only CF4/O2 plasma RIE was used to etch away diamond nanoparticles, is shown in Fig. 2a. Isolated and randomly distributed residual diamond crystals were observed on unintended areas, i.e., the areas not protected by the polymer photore sist. The density of residual crystals in this case was up to $8 \times 10^6$ cm$^{-2}$ as calculated using the Atlas software. It should be noted that the diamond growth in unintended areas is also called as the parasitic growth characterized by parasitic densities, i.e., the number of diamond grains per unit area.

Figure 2b shows diamond structures grown by the strategy B. The sandwich-like structure of polymer–seeding–polymer layers processed by optical lithography resulted in a lower selectivity than the treatment strategy A. The parasitic density was as high as $5 \times 10^7$ cm$^{-2}$.

Diamond structures formed by the strategy C are shown in Fig. 2c. In this case, the density of residual diamond crystals reached the lowest value – $10^5$ cm$^{-2}$.

AFM images (data not shown) well agreed with SEM measurements. The height (thickness) of the diamond stripes was nearly the same for all the sample sets. It was about 520 nm as deduced from AFM height histograms.
Characteristic Raman spectra of the structures are presented in Fig. 3. Measurements from on-stripe areas for all the samples reveal a dominant peak centered at 1332 cm\(^{-1}\), which confirms the diamond character of these stripes [9]. A sharp peak centered at 520 cm\(^{-1}\) is assigned to the Si substrate. In addition, three broad bands were detected: one centered at 1180 cm\(^{-1}\), which is assigned to transpolyacetylene segments at grain boundaries, and two broad bands centered at 1367 and 1575 cm\(^{-1}\), which are attributed to sp\(^2\) carbon phases labeled as D (disorder) and G (graphitic) bands, respectively [10].

Raman measurements on the bright dots in the off-stripe areas also reveal the characteristic diamond peak. Dark regions in the off-stripe areas exhibit only the substrate characteristic peak. In this case, the intensity of diamond peak was under the detection limit of our measurement setup. These results enable us to analyze SEM images in the terms of diamond growth selectivity and confirm that the strategy C leads to the best selectivity.

All used strategies resulted in the direct growth of diamond structures. Obtained results indicate that the main differences are in the initial patterning of the seeding layer.

A crucial limitation of the strategy A is masking polymer that exhibited low resistance to the plasma treatment. For our RIE conditions, the polymer sustained maximally 5 min. Unfortunately, this etching period was not long enough to etch all the seeds. Some diamond seeds survived the plasma treatment and initiated growth of large diamond crystals in unintended areas. During ultrasonic seeding some areas also contained clustered grains that are more resistant to the plasma etching. Their removal requires prolonged etching time which can damage and/or destroy the top surface of the substrate surfaces. In addition we observed that prolonged etching period resulted in damaging the structures protected by the polymer. Consequently, the growth of porous diamond structures was observed in those areas. Previously it was shown that metal mask allowed a prolonged plasma etching time up to 20 min, see the work of Bongrain et al. [2]. In such case, the residual density of parasitic crystal decreased down to \(5 \times 10^5\) cm\(^{-2}\). However, using metal mask requires its selective removal from the seeding layer before the CVD growth. This is mostly provided by wet-chemical etching which can damage the seeding layer. Thus following CVD diamond growth will result in pinholes in the diamond structures. In our case, applying thicker polymer layer should help in prolonging the plasma etching step.

In strategy B (Fig. 1 – set B) sandwich-like structure was firstly irradiated by UV light and then both polymer layers were selectively removed by appropriate solvent. During this dissolution, diamond seed packed between polymer layers should be removed. Unfortunately, relatively high amount of residual diamond crystal was still detected. We attribute it to the sedimentation of diamond seeds (i.e., re-seeding) during chemical dissolution of the photoresist. We observed that turning the sample upside down in solvent partially decreased the density of remaining diamond seeds.

For the strategy C, treatment is technologically more complex. First, similarly as for strategy B, the UV irradiation and development in the solvent were prolonged due to using two polymer layers. Thus, the “top” photoresist layer decreased its thickness. Consequently, a shorter plasma etching (3 min) was applicable in comparison with the
treatment in the set A. However, the strategy C resulted in more effective decrease in the parasitic density of diamond crystals. Removing of the seeds was provided in two steps: (i) during dissolution of polymer layers (similarly as in the set B) and (ii) by RIE (similarly as in the set A). We observed that short RIE is better for SAD growth. In this case shorter plasma treatment is gentler than in the case of the set (A) where applying RIE for 5 min was still not efficient enough to achieve a good SAD growth. Strategy C employs two gentle treatments which are more favorable for mechanically and chemically sensitive substrates.

Noticeable feature of the strategy B and C is the fact that the seeding diamond layer was packed in the “polymer” sandwich-like structure which has not been removed prior to the diamond CVD growth. During the chemical vapor deposition, polymers can act as additional carbon source for diamond CVD growth and the rest is removed (etched) in relatively aggressive plasma environment mainly consisting of atomic hydrogen. On the other hand, slow etching of sp² bonded carbon from polymer can result in its higher content at the substrate–diamond interface. We assume that the presence of D and G bands in the Raman spectrum collected from the “on-stripe” area can be attributed to a lower quality of diamond in the early stage of growth. Contrary to this observation, Raman spectrum collected from “off-stripe” area of sample prepared by strategy B (i.e., no polymer but only a residual diamond seeds were present) exhibited only a diamond characteristic peak (Fig. 3 – bright dots in the off-stripe area).

Strategy C was successfully used for patterned growth of diamond micro-channel structures which exhibited good enough surface properties for fabrication of electronic devices as field effect transistors. Figure 4 represents an AFM pattern of such channel structure with following dimensions: 20 μm in width, 60 μm in length, and 600 nm (±30 nm) in height.

Our previous I–V measurements confirmed that directly grown diamond channels are well suitable for realization of solid or liquid gated FETs. Channel current, i.e., 2D hole carries induced in the diamond subsurface due to hydrogen termination, was modulated by applying gate voltage along the complex 3D geometrically defined diamond structure [11].

The main advantages of all above described strategies are: (i) omitting any destructive treatment of substrate, e.g., its rinsing in acid to remove metal mask [1, 2], (ii) easy applications on large-area substrates, (iii) suitability for diverse substrate materials, and (iv) compatibility with standard semiconductor processes.

4 Conclusions We have investigated SAD of CVD diamond structures applying three different strategies that avoid treatment by aggressive chemistries. Strategies A and B resulted in a clear difference between the diamond growth in intended (on-stripe) and unintended (off-stripe) areas. Yet the density of parasitic diamond crystals was still too high for fabrication of electronic devices like field effect transistors. The combined strategy C resulted in the best selectivity of diamond structure formation. The residual density in unintended growth areas was decreased down to 10⁵ cm⁻² that is close to a general theoretical limit. Although a short RIE step is still essential, the strategy C opens new pathways for well selective direct growth of diamond microstructures on diverse substrate materials.

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