Selective deposition of polycrystalline diamond films using photolithography with addition of nanodiamonds as nucleation centers

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Abstract. A new method of selective deposition of polycrystalline diamond has been developed and studied. The diamond coatings with a complex, predetermined geometry and resolution up to 5 μm were obtained. A high density of polycrystallites in the coating area was reached (up to $32 \cdot 10^7$ pcs/cm2). The uniformity of the film reached 100%, and the degree of the surface contamination by parasitic crystals did not exceed 2%. The technology was based on the application of the standard photolithography with an addition of nanodiamond suspension into the photoresist that provided the creation of the centers of further nucleation in the areas which require further overgrowth. The films were deposited onto monocrystalline silicon substrates using the method of "hot filaments" in the CVD reactor. The properties of the coating and the impact of the nanodiamond suspension concentration in the photoresist were also studied. The potential use of the given method includes a high resolution, technological efficiency, and low labor costs compared to the standard methods (laser treatment, chemical etching in aggressive environments).

1. Introduction

Nowadays, the interest to the field of application of various new and better materials in semiconductor electronics is actively growing. One of the promising materials seems to be a diamond. This material is different from the others by a large number of parameters, which are extreme and necessary for semiconductor electronics [1], such as the highest thermal conductivity of all solids (900-2300 W/m·K), chemical and radiation resistance, and a wide bandwidth of the optic radiation from the deep ultraviolet to the far infrared. Pure diamond is a good electrical insulator (specific resistance ~10^{16} Ω·cm at room temperature), during doping of diamond its specific resistance can change over a wide range from 10 to 10^6 (Ω·cm), that turns it into a wide-gap semiconductor with a 5.4 eV band gap. The coefficient of thermal expansion (CTE) of the diamond is one of the lowest and at room temperature it can be compared to CTE of invar ($0.8 \cdot 10^{-6}$ K) [1, 2].

Despite these advantages, there are a lot of technological problems in the mass use of diamond in electronics, which complicate its application and impose restrictions on its use in industrial processes. Due to the nature of synthesis and high complexity of processing a monocrystalline diamond, it is difficult and low-tech to create the electronic structures with a complex geometry based on it,

especially with the size applicable in micro- and nanoelectronics [1, 3]. Therefore, the application of the diamond in the form of polycrystalline films, which can be deposited onto homo- and getero-substrates, seems very promising [4].

The main problem for their use is the lack of the advanced technology of their selective deposition, which is extremely necessary for the construction of microelectronic devices. Most of the existing methods of creating the necessary topology of semiconductor structures are almost inapplicable for diamond. Wet etching of structures using direct and lift-off stencils is complicated by the fact that using highly aggressive etchants at high P-T parameters is unacceptable in semiconductor electronics. Using the lift-off stencils is limited by the fact that the high density of the diamond does not allow the diamond layers to delete over the etched material, and only the cavities under the film are etched off [5]. The surface laser treatment of the diamond films can be more applied to the ablation treatment (roughness alignment) and cutting, because of high power applied and low controllability of the depth [6]. Ion etching in different atmospheres is hardly applicable because of low efficiency and long duration of the etching process [7].

The use of high purity natural diamond is very expensive and time consuming, and there only tiny crystals in small quantities can be obtained. The use of synthetic diamond enables to simplify the process and to reduce its cost, but its manufacture still requires high-purity diamond substrates, and crystal growth is very limited in size and geometry. In addition, its further processing is complicated, because the use of the conventional methods of etching, grinding, etc., is ineffective due to resistance of diamond to various influences [1]. Using the polycrystalline diamond enables to obtain the films on the substrates with a similar structure of the crystal lattice that enables to avoid the use of expensive and small diamond samples. At the same time, this type of diamond, though slightly ranks below classic diamond, i.e. monocrystalline one, still provides the parameters unapproachable to the other materials, combining it with a higher technological effectiveness of its production and application [1, 3].

This paper proposes a radically different method of growing polycrystalline diamond films, which enables the selective deposition of the films with predetermined parameters of geometry and shape.

2. Experimental

Using the conventional method of producing the growth nucleation centers due to the ultrasonic treatment of silicon wafers in the nanodiamond suspension [8] does not enable to obtaine a required pattern without using a complex and non-technological further processing. The proposed method of obtaining a pattern by creating nucleation centers only in the required areas by applying a photoresist with an addition of nanodiamonds and creation of the required topology using photolithography enables to determine the film geometry before its growth.

In our work, we studied the films obtained by the conventional method and the films obtained with photoresist with different concentration of diamond nanoparticles by weight. The photoresist was prepared by adding 5/10/15 (% by weight) suspension of nanodiamonds (3% by weight). That enabled to produce photoresists with a concentration of nanodiamonds of 0.15/0.30/0.45 (% by weight), respectively.

In the technological process we used: silicon wafers (SW) of 76 mm in diameter, 350-400 μm thick and (111) orientation, photomask (PM) with a suitable pattern, a positive photoresist (SP-051 SU-05) mixed with diamond nanocrystals in the required proportions (0.15, 0.30, and 0.45 % by weight).

The first phase was chemical cleaning of the wafers from contamination in ultrasound. Then, the photoresist was applied using centrifugation, which caused the formation of the photolayer. After that, SW was dried in an oven at a temperature of 70-90°C for solidification of the photoresist. The wafer was aligned with PM followed by layer exposure at the AMK 2104.16 by UV with λ = (250-440) nm. The photolayer was developed in alkaline solution (KOH) and then further developed using plasma treatment in the nitrogen atmosphere. And at the final stage the obtained silicon wafer was finally dried in the oven at 120-140°C.

Table 1. The main operating parameters

Temperature of filament	Temperature of wafer	Working pressure	Deposition rate	Distance to wafer
2000±50°C	800±25°C	20±1 Torr	0.5 μm/h	10 mm

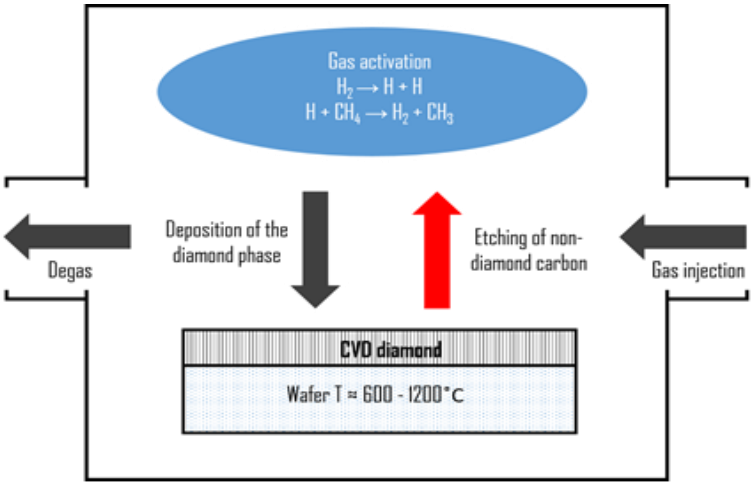

Figure 1. Diagram of the diamond deposition

During the film deposition, we used a specialized CVD reactor. The reactor is based on a well-known method of "hot filaments" [9, 10]. In this method, the gas mixture (H_2/CH_4) is activated thermally using hot tungsten filaments. The temperature of tungsten filaments (0.2 mm in diameter) was 2000±50°C (measured using the infrared pyrometer) in the reactor. The pressure during the film deposition was 20±1 Torr at a methane concentration in hydrogen 2 %. The distance from the wafer to the filaments was constant at 10 mm.

3. Results and discussion

The phase composition and the purity degree of the synthesized diamond films were determined using the most accurate method, i.e. Raman spectroscopy (NanoScan Technology Centaur I HR spectrometer). Figure 2 shows the Raman spectrum obtained in the area of the solid film. It is close to the spectrum characteristic to monocrystalline diamond. The line width, which characterizes sp^3-carbon (1333 cm^{-1}), is less than 50 cm^{-1}, which indicates the absence of amorphous sp^3-carbon. The lines of the parasitic inclusions typical for polycrystalline diamond [11] (lines of trans-PA (1450 cm^{-1}) and G band of graphite (1560 cm^{-1})) are also not observed in the spectrum. Thus, the deposited films consist of high-quality diamond material and the photoresist does not make any significant impurities in them.

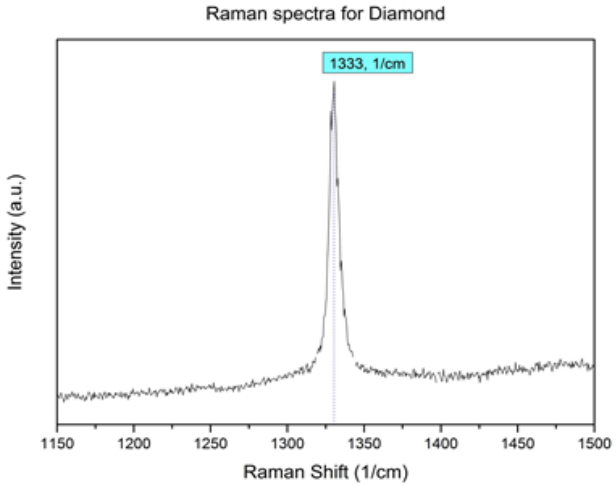

Figure 2. The Raman spectrum of the deposited diamond films

The topology and uniformity of coatings was analyzed using scanning electron microscopy (FEI Quanta 3D SEM) without adding additional conductive layers. The micrographs in Figure 3 show that the method enables film selective deposition, despite the presence of a certain number of "parasitic" crystallites formed in the area, where nanodiamond-containing photoresist was removed before deposition. The creation of these crystallites can be explained by the fact that when photoresist was washed off in the non-exposed areas, some nanodiamonds still remain on the silicon and during deposition they serve as nucleation centers for "parasitic" crystallites. This effect increases with increasing the concentration of nanodiamonds in the photoresist that is demonstrated by the comparison in Figure 3 (a, b, and c) (the content of the nanodiamond is 0.15, 0.30, and 0.45 wt.%, respectively).

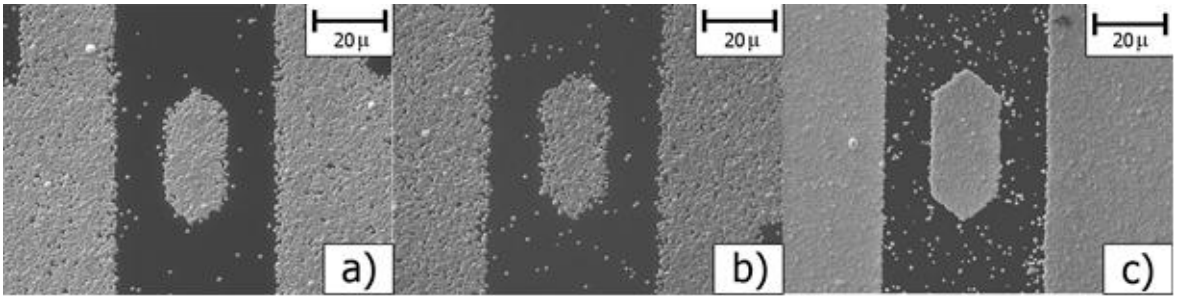

Figure 3. SEM micrographs of selectively deposited diamond films on monocrystalline silicon with different mass content of nanodiamond in the photoresist: a) 0.15%; b) 0.30%; c) 0.45%

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uniformity. Thus, the comparison of the film surfaces on the samples prepared with nanodiamond content of 0.15 and 0.45 wt.% (Figures 3a and c) shows that the average concentration of the crystallites is significantly different. The samples, where the selective seeding was carried out at a low content of nanodiamonds, take much more time to form a uniform film, and hence the average crystallite size in such films is significantly higher, that seriously reduces the resolution of this method of selective deposition.

Table 2. Diamond film concentration and uniformity versus the amount of nanodiamond particles in the photoresist

Mass fraction of nanodiamond in photoresist, %	Average concentration of crystals in film	Average concentration of crystals in "clean"	Average uniformity of film coating	Average uniformity of "clean" area

	(pcs/cm^2) × 10^7	area (pcs/cm^2) × 10^6	(%)	surface (%)
0.15	7.98	1.06	91.73	1.22
0.30	9.88	1.94	94.86	1.86
0.45	31.9	5.71	100	2.01

Table 2 shows the comparative statistical data on the dependences of the film uniformity and the diamond crystallite concentration on the amount of the nanodiamond particles in the photoresist. As it is seen, the higher concentration of the nanodiamond produces the films using smaller crystallites and a more accurate pattern, but the number of "parasitic" crystals in the "clean" area increases proportionally.

4. Conclusion

During this work the polycrystalline diamond films of high purity were obtained on the monocrystalline silicon wafers and at the predetermined surface geometry by selective deposition of photoresistive layers with nanodiamond particles using a conventional industrial photolithography. The obtained films, already at this stage, can be applied as a protective layer for devices, which require the coatings with improved properties of strength and chemical resistance. It is possible to simplify the cutting and processing of the required diamond films through selective pattern. Increase in the concentration of nanodiamond in the photoresist increases the uniformity of the films and decreases the average size of the crystallites in them, but also causes an increase in density and "parasitic" diamond nuclei in the areas, which should be free from films. Thus, we can conclude that this technique requires further development to completely eliminate the formation of the unwanted nucleation centers to be widely applied in microelectronics as layers of electronic component of the device (dielectric, semiconductor, etc.).

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