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Research of Influence of Different Preparation Parameters on Secondary Electron Emission of a Single Crystal Diamond with the Purpose of Microchannel Devices Development with High Quantum Efficiency

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Abstract: Possibility and advantages of use of a single crystal diamond (HPHT and CVD) as highly effective secondary emitter are shown in this paper. The maximum secondary electron emission (SEE) coefficient about 14 at working accelerating voltage is received (several times exceeds SE coefficient of used materials, such as silicon), lack of dependence on diamond type is shown, dependence on current of primary beam is revealed. The main goals of experiments were to establish optimal characteristic of primary beam (such as energy of primary beam and current) and sample preparation for achievement the maximum coefficient of secondary electron emission (SEE coefficient). Experimental data were analyzed and an optimum technique of preparation of a diamond samples surface for use as secondary emitters was developed. Taking into account outstanding diamond characteristics there is a possibility for creation unique and highly effective detectors and converters based on effect of SE. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Secondary Emission, Electron affinities, Diamond, Surface states, Microchannel devices.

1. Introduction

Wide band gap materials have attract much interest as materials with high quantum efficiency due to their low or negative electron affinity (NEA), when the bottom of a conduction band is above vacuum level, so low-energy electrons in conduction band should be emitted in vacuum without energy loss.

In general, metals and semiconductors are relatively poor secondary-electron emitters, but wide band gap materials (insulators), on the contrary, are very good in this effect [1]. Carbon provides an excellent example in this tendency. For example, carbon in graphitic form is one of the poorest secondary-electron emitters: the maximum SEE coefficient is about 1.0 for graphite and 0.45 for soot [2]. But diamond, wide band gap material, exhibits an unusually high SEE coefficient: in some articles authors report that the SE coefficient of single crystal diamond is about 100 [3]. For comparison, a table of the coefficient of SEE from insulators shows that the previously known highest value is 23, measured on crystalline MgO [1].

Recent researches in the field of a single crystal diamond growth made this material cheaper.

CVD process is actively used now for production depreciation. The fact that price has dropped allows us to use diamond more widely for creation modern electronics with outstanding characteristics.

Therefore, use of diamond as highly effective multiplier of electron current looks perspective.

2. Description of Diamond Samples and Measurements

In this paper we investigated different types of diamond: various levels of concentration of boron (type IIb) and nitrogen (type Ib), various orientation directions, free and hydrogenated diamond surfaces, samples grown by using HPHT and microwave-plasma CVD methods. CVD diamonds were grown by use HPHT diamond single crystal substrates.

For the first experiment the following samples were prepared (Table 1):

Table 1. Diamond sample comparison.

No.	Type	Orientation	H-termination
1	IIb	(001)	Yes
2	IIb	(001)	No
3	IIb	(001)	No
4	IIa	(110)	Yes
5	IIa	(001)	No

Thickness of a diamond plates was in limits from 300 microns to 500 microns. Thus, thickness of plates exceeded interaction depth with primary electron beam and secondary electron emission from a diamond plate was measured. All samples were polished, consistently washed in acetone and isopropyl alcohol. Samples with free surfaces were washed and polished the same methods.

It is known that surface properties of diamond essentially depend on preparation methods and sequence of operations. Annealing in the atmosphere of hydrogen changes physical and chemical properties of diamond surface. It's called H-termination and is characterized by negative electronic affinity appearance when the bottom of conductivity band is above vacuum level. It is expected that such preparation can significantly improve SEE from diamond since there will be no energy dissipation of electron output from a conductivity band to the vacuum.

Thus, some of diamond plates were terminated by hydrogen (H-termination) in CVD system. The following mode of annealing was chosen: first off all, heating from room temperature to 800 °C during 30 minutes, then plates were kept at 800 °C during 5 minutes and the subsequent cooling. This sample preparation allowed to compare coefficients of secondary electron emission of H-terminated samples and samples with free surface.

Scanning electronic microscopes FEI Quanta 200 and Tescan Vega 3 SBH were applied for this study, which allowed to use all required range of energy (from 200 eV to 30 keV) of primary electron beam, had necessary outputs for measurements, movements of positional table on five independent axes (X, Y, Z, rotation and turn with high precision) and standard detector of true and secondary electrons for visualization of areas with various coefficient of secondary electron emission.

Possibilities of use of various measurement schemes were investigated, but the best one for low-energy electrons measurement and the best shielding from undesirable EM-noises on measuring wires and devices was in the scheme specified in Fig. 1. In this figure I_{beam} is a total current from SEM, I_{SE} is a secondary electron emission current, U_{bias} is a shift voltage, I_{abs} is a current via ammeter.

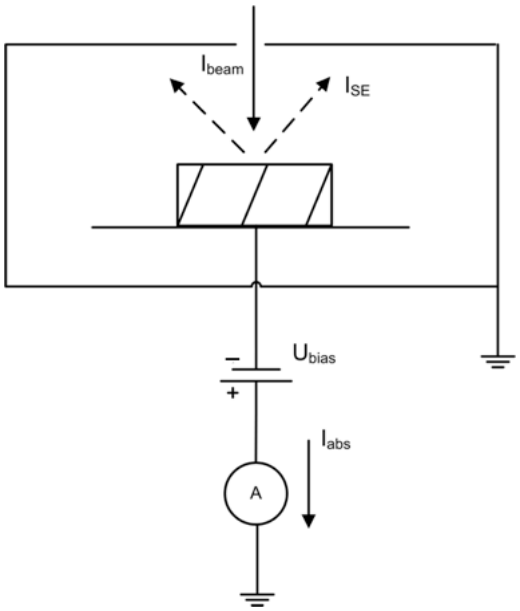

Fig. 1. Scheme model of experiment.

The set of various detectors (detectors of secondary and the low-loss electrons, X-ray and optical quanta, the screen for electronic diffraction, etc.) is installed in the microscope with their own power supply or voltage shift, so a distribution of electric field inside chamber is very difficult to calculate. Therefore, it's impossible to predict a trajectory of movement of secondary electrons in advance. In order not to consider influence of internal elements of a design of a microscope on collecting secondary electrons, the grounded screen near a sample was installed.

During research of samples with insufficient conductivity accumulation of a surface charge near interaction area of a primary beam with a sample is possible. For example, if coefficient of secondary electron emission is more than 1.0, a surface of a sample charges positively. So, surface charge distorts

local distribution of electric field near interaction area. This field tries to return the secondary electrons back. Low-energy electrons with kinetic energy less than 100 eV prevail in the range of secondary electrons owing to their energy distribution. Thus, existence of positive charge on a sample surface can significantly distort measurements of coefficient of SE since we can't measure a beam of secondary electrons which return back to a sample. This process is shown in Fig. 2. To minimize influence of charging on collecting secondary electrons was offered to apply negative potential of shift.

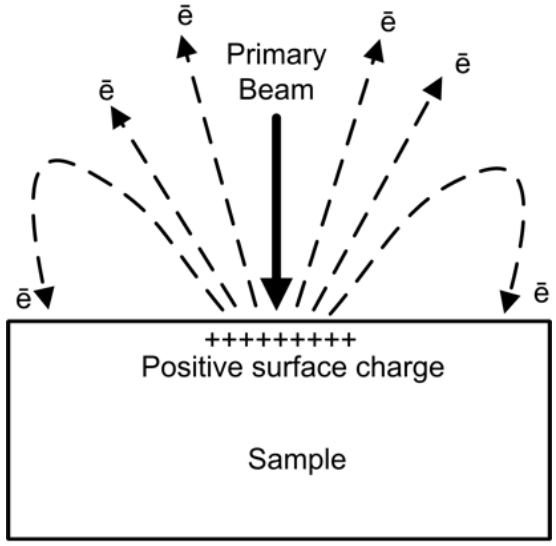

Fig. 2. Process of surface "charging" of a sample.

During the measurements the electron gun of SEM creates a beam of primary electrons and described by I_{beam}. Secondary electrons are beaten out to the vacuum from its surface layer at interaction point of primary electron beam with a sample. This beam is described by I_{SE} current. If we measure the absorbed current I_{abs}, i.e. to measure current transmitted through a table, according to Kirchhoff's law we can calculate:

$$I_{abs} = I_{beam} - I_{SE} \quad (1)$$

The current of secondary electrons is

$$I_{SE} = I_{beam} - I_{abs} \quad (2)$$

And, respectively, a coefficient of secondary electron emission equals:

$$K_{SE} = \frac{I_{SE}}{I_{beam}} = \frac{I_{beam} - I_{abs}}{I_{beam}} = 1 - \frac{I_{abs}}{I_{beam}} \quad (3)$$

Value of primary beam current remains only conditionally constant therefore after accelerating voltage is changed, current of a beam must be controlled by means of Faraday cup. Negative shift in the scheme was made by constant battery of 40 V. Values of currents were measured by using source meter Keithley 2612A.

3. Secondary Electron Emission Measurement

3.1. Confirmation of SEE Diamond Properties and Characteristics

Efficiency of secondary electrons creation was estimated by analyzing of brightness of the image received from built-in detector of true-secondary electrons. In Fig. 3 images of samples No. 1, No. 2 and No. 3 are given, in Fig. 4 – No. 4 and No. 5.

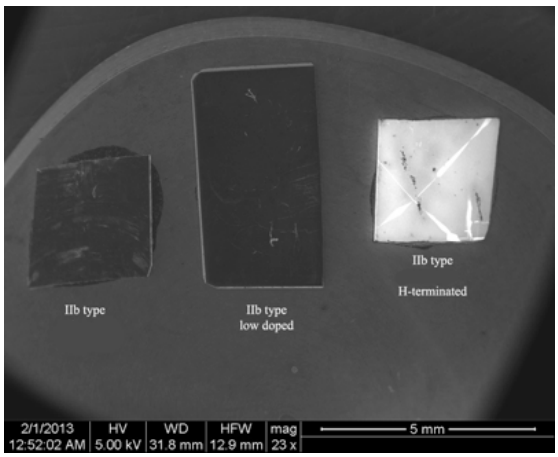

Fig. 3. Comparison of secondary electron emission efficiency from IIb diamonds.

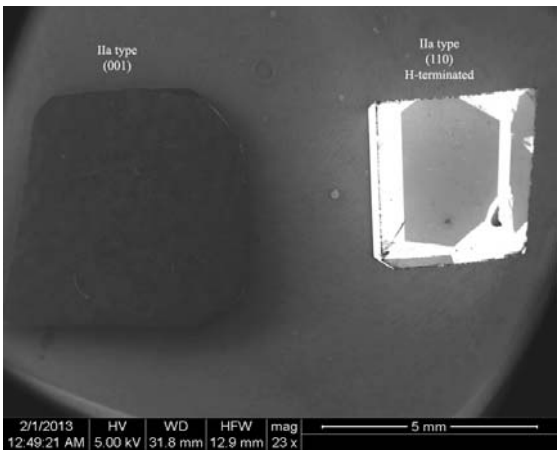

Fig. 4. Comparison of secondary electron emission efficiency from IIa diamonds.

Figures, assumptions of increasing of SEE coefficient using diamond surface H-termination process completely were confirmed. Thus, the observed increase occurs both on high-pure dielectric

and the boron-doped conductive samples. Also it should be noted that after H-termination the areas of diamond growth were easily observed in the picture of SEE.

Further measurements of dependence of SEE coefficient (according to the scheme shown in Fig. 1) on current of primary beam were carried out at two values of accelerating voltages of 1 kV (Fig. 5) and 10 kV (Fig. 6). It's shown that both samples, which surfaces were H-terminated, have coefficient of SEE 4-5 times higher, than other samples with an unprepared surface. Thus, the difference in SEE between boron-doped and high-pure diamonds isn't revealed. It's important to note that we found dependence of SEE coefficient on current of primary beam on both samples with H-termination.

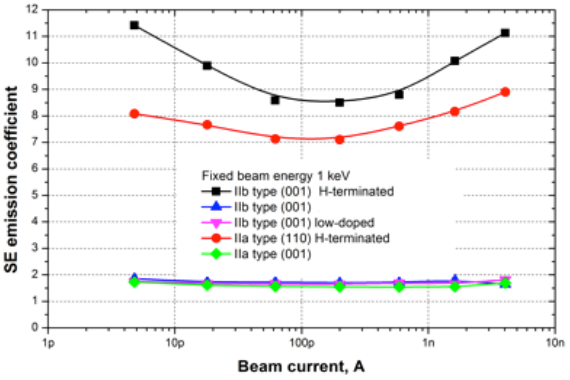

Fig. 5. Dependence of secondary electron emission coefficient on current of primary beam (beam energy 1 kV).

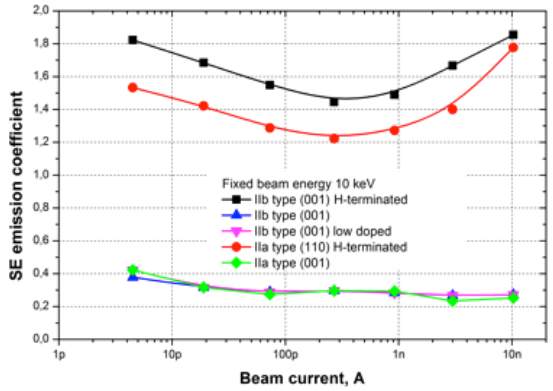

Fig. 6. Dependence of secondary electron emission coefficient on current of primary beam (beam energy 10 kV).

Also attempt to measure dependence of SEE coefficient on an angle of primary beam of electrons was made. However, the received dependence differs from theoretically expected (see Fig. 7). This discrepancy can be explained by change of a sample area analyzed during rotation. Thus, for the next area real value of SEE can differ or can have another condition of charging.

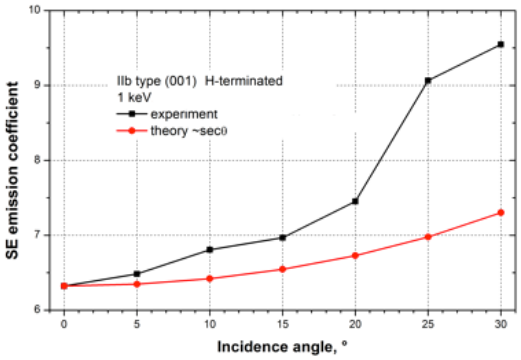

Fig. 7. Dependence of secondary electronic emission coefficient on an angle of primary beam.

3.2. Investigation of Dependence of SEE Coefficient from Temperature Changes of H-termination

For the second experiment the following samples were prepared (Table 2):

Table 2. Diamond sample comparison.

No.	Type	Orientation	H-termination
1	IIb	(001)	Yes
2	IIb	(001)	Yes
3	IIb	(001)	Yes
4	IIb	(001)	Yes
5	CVD	(001)	Yes, in the process of growth

Methods of preparation were as in the previous experiment, but temperature of process changed in range from 475 °C and to 850 °C.

Using the scheme shown in Fig. 1, dependence of SEE coefficient on the primary electron energy were established. The comparative plot for diamond samples in all range of the accelerating voltages available on SEM Tescan Vega 3 SBH was graphed. Results are shown in Fig. 8.

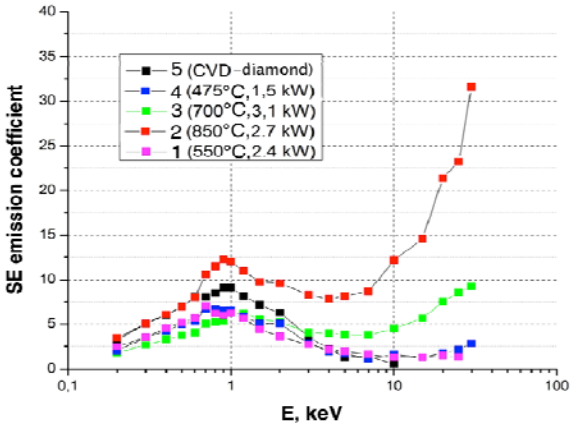

Fig. 8. Comparative analysis of secondary electron emission coefficients.

During the analysis of the results presented on the plot it is possible to specify the location of SEE maximum which was located in the range of primary beam energy from 0,8 keV to 1,1 keV. The location scatter of a maximum is caused by a measurement error and imperfection of the scheme: the screen of a constant source of voltage (battery) was made of aluminum foil and had very poor contact with ground, respectively, there were errors in results of measurements.

The measured maximum SEE coefficients: the sample No. 1 ≈ 7; the sample No. 2 ≈ 12.3; the sample No. 3 ≈ 6.3; the sample No. 4 ≈ 6.7; the sample No. 5 ≈ 9.1.

In addition it should be noted high (in relation to other samples in experiment) SEE coefficient at the sample No. 2. This fact can be explained by the highest temperature of H-termination process and also by chosen area of measurements – the glowing center in Fig. 9.

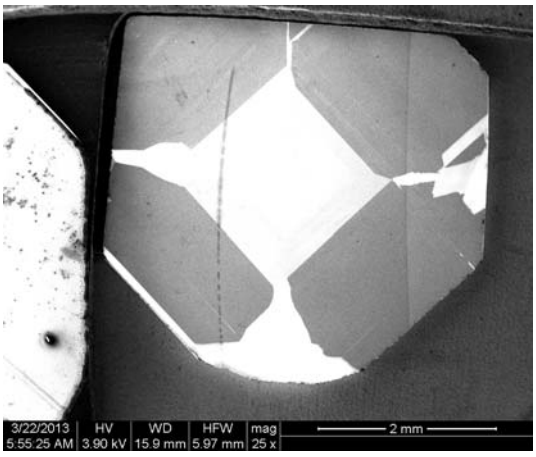

Fig. 9. SEE intensity distribution of the sample No. 2.

It is necessary to note an existence of dependence of SEE coefficient from temperature of process of H–termination. When the process temperature was higher, secondary electron emission coefficient was higher too at the same accelerated voltage.

3.3. Investigation of Dependence of SEE Coefficient from Power Changes of H-termination

For the third experiment the following samples were prepared (Table 3).

Samples No. 1 and No. 2 were taken from the previous experiment, no additional preparation were made and, accordingly, stayed for 1 month on air.

Using the improved scheme, the comparative plot of dependence of SEE on the accelerating potential was graphed. Results are shown in Fig. 10.

Table 3. Diamond sample comparison.

No.	Type	Orientation	T, °C	Power, kW
1	IIb	(001)	-	-
2	IIb	(001)	-	-
6	IIb	(001)	1100	3
7	IIb	(001)	1200	3,25
8	IIb	(001)	1100	3,35

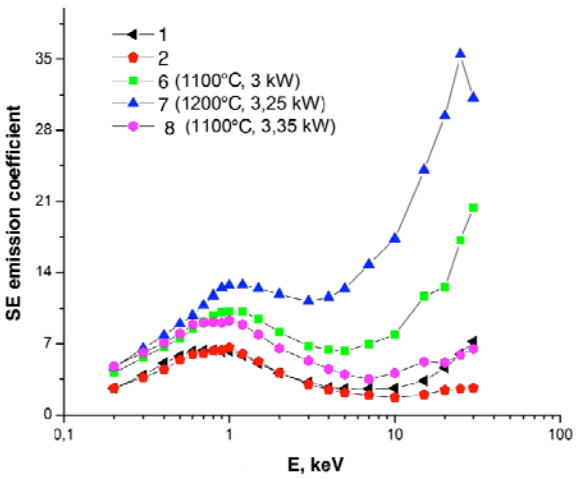

Fig. 10. Comparative analysis of secondary electron emission coefficients.

Comparing these results to the results received earlier (a month before it) for samples No. 1 and No. 2 it is important to notice considerable decrease of SEE (for a sample No. 2) more than by 1.5 times. This fact can specify a degrading of a hydrogen layer. In addition, it should be noted that samples were stayed on air without any special storage conditions. Also from this plot it is possible to draw a conclusion on a greater influence of temperature to hydrogenation process, than plasma power.

4. Conclusions

Thus, possibility of creation of highly effective secondary emitters for development of the advanced electronics is shown. But the set of questions and technical details remain undecided and require further research. So, we can make microchannel plates of a single-crystal diamond with outstanding physical characteristics.

Acknowledgements

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