*PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES*
Vol. **1** No 4, 04PITSE08(3pp) (2012)

# Plasma Processing Reactor on a Base of Beam Plasma Discharge for Producing and Processing Nanomaterials

E.G. Shustin*, N.V. Isaev, I.L. Klykov, V.V. Peskov

*V.A. Kotelnikov Institute of Radio Engineering a. Electronics of RAS, Fryazino Branch*
*Vvedensky Sq. 1, Fryazino, Moscow reg., Russia*

(Received 20 June 2012; published online 24 August 2012)

The paper describes the design, modes and applications of novel kind of low pressure plasma processing reactor based on beam plasma discharge as the plasma source. This reactor ensures flawless treatment of material surface as well as deposition of specific coatings with strictly defined energy of ions acting upon a treated surface. Applications of the reactor are represented such as defect-free etching heterostructures based on GaAs and producing structurally perfect samples of graphene.

**Keywords**: Plasma processing reactor, Beam plasma discharge, Etching, Deposition, Graphene.

PACS numbers: 52.77. – j, 52.80.Tn

## 1. INTRODUCTION

Different plasma assisted processes are widely used for the production of a broad spectrum of semiconductor devices. There are two kinds of tasks for plasma technologies in nanoelectronics: surface treatment of thin films and heterostructures (cleaning, patterning, and implantation) and deposition of nano-dimensional semiconductor and dielectric films. These problems are currently solved mainly by technologies with low pressure plasma sources which are varieties of UHF discharge. One of the major problems arising especially at moving to the field of nanoelectronics is soft defect-free anisotropic etching of semiconductor and dielectric structures. Solving this problem in the traditional plasma processing reactors based on UHF discharge runs into considerable difficulties.

This report is a review of the work on creation of novel kind of low pressure plasma processing reactor both for flawless treatment of material surface and for deposition of carbonaceous films. This type of reactor is based on effect found earlier [1] of generating ion flows with energy up to several tens volts which propagate from a beam plasma discharge (BPD) on normal to its axis.

## 2. REACTOR DESCRIPTION

The reactor scheme is shown on Figure 1 [2]. Plasma is created in a vacuum chamber which is a cylinder with diameter 0.5 m and the same length due to beam plasma discharge. Argon pressure ~ 0.05 Pa is kept in the chamber. A diode electron gun of Pierce type with $LaB_6$ cathode is applied as the source of an axial electron beam. Parameters of the electron beam at the plasma chamber entrance are: accelerating voltage is 2 kV, beam current is 0.3 – 0.5 A, diameter on the chamber entrance is ~ 1 cm. The power supply ensures the gun work in a pulsed mode with pulse duration $\tau_b$ = 10 – 200 ms, repetition frequency 1 Hz. A discharge collector is placed near an opposite wall of the plasma chamber. An electrostatic analyzer with a flat deflecting mirror is used as a detector of the ion flux.

Experiments have shown that, by changing parameters of BPD in the equipotential interaction chamber, it is possible to change the mean energy of an ion flow that arrives at a surface near to a side wall of the chamber, in the range 8 – 40 eV. The flow density was about 0.1 mA/cm² under these conditions. The zone with maximum flow density and mean energy is localized and has size along the axis ~ 60 – 100 mm. The position of this zone depends on the gas pressure. We have revealed that a highly non-equilibrium plasma with mean energy of electrons up to several hundred eV is formed in the area occupied by the beam as a consequence of excitation of stochastic oscillations in the area of the discharge and collisionless adsorption of these oscillations. Enhanced electron current from this area causes growth of plasma potential in the paraxial region normal to the axis of the system.

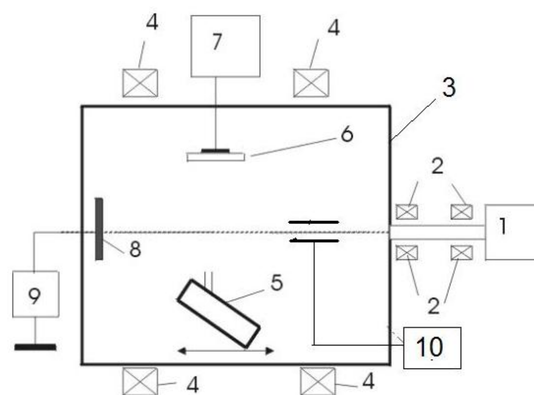



**Fig.1** – Diagram of installation. 1 – electron injector, 2 – focusing coils, 3 – vacuum chamber, 4 – Helmholtz coils, 5 – ion energy analyzer, 6 – substrate holder, 7 – power supply for holder heater, 8 – collector, 9 – voltage supply, 10 – supply of modulating electrode

The revealed mechanism of ion acceleration has led to the conclusion that simple control of density and energy of the ion flow could be realized by changing the

* shustin@ms.ire.rssi.ru


© 2012 Sumy State University

discharge collector potential. Indeed variation of the collector potential in the range 0 – 150 V results in change of the ion mean energy from 20 up to 120 eV with increase of flow density by an order of magnitude (see Fig. 2).

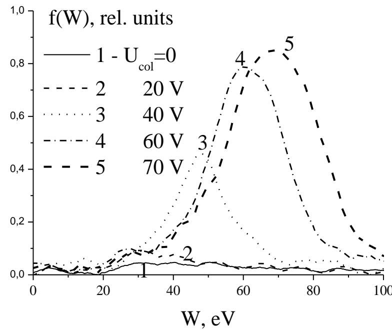



**Fig. 2** – Ion energy distribution function at various collector voltages.

At processing a non-conducting surface with an uncompensated ion flux a floating potential of the surface is created which retards ions (see Fig. 3). We proposed to use pulse modulation of the collector potential for controlling the plasma potential [3]. Since ion fluence and a floating potential of an isolated surface obviously depend on the plasma potential, its modulation with alternating signal will create periodic neutralization of the charge.

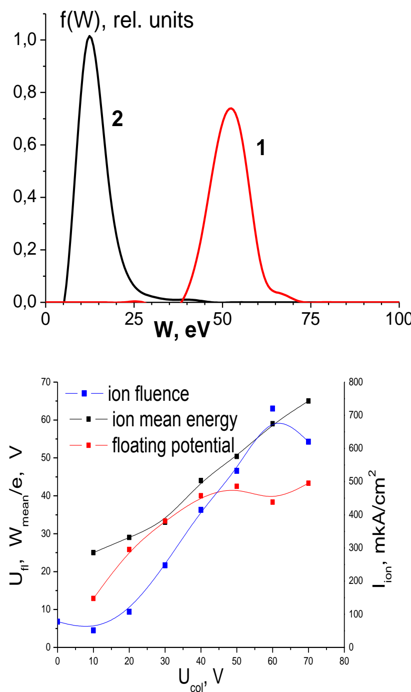



**Fig. 3** – IEDF curves for conducting ion receiver (1) and for isolated one (2) (computer simulation) (top). Ion flow parameters at the chamber wall jointly with floating potential of the receiver 2 vs. collector potential (experiment) (low)

A high frequency modulator has been designed for this mode. The modulator provides generation of pulsed voltage with amplitude 30 – 150 V at load current ≤1 A in the range of operating frequencies 100 – 400 kHz. Its pulse has the leading edge 50 – 75 ns, the falling edge 150 – 250 ns. The modulator can operate at duty ratio ≥ 2. Special experiments with probes which simulate surfaces of isolating substrates [3] have shown that energy of ions acting upon the treated surface is close to $eV_p$ (where $V_p$ is amplitude of the pulse voltage of the collector) and varies rather little during the pulse, provided that the probe capacitance is close to the capacitance of substrates used commonly. At the trailing edge of the pulse a discharge of the surface occurs at a rate a little lower than the slope of the trailing edge.

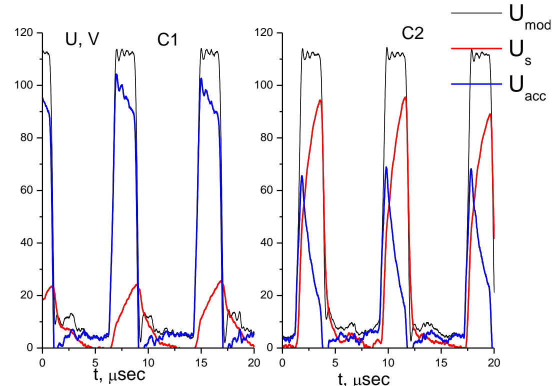



**Fig. 4** – Potential Us of isolated surface at pulse modulation of collector voltage and various probe capacitances: *C1* = 60 pF/cm2; *C2* = 6 pF/cm2. The discharge parameters are typical for the etching mode. Uacc = Umod-Us is voltage accelerating ions

## 3. REACTOR APPLICATION

The range of energies of the argon ions (20 – 70 eV) is optimum for flawless sputtering compounds such as AIIIBV and heterostructures based on these compounds. Hence etching heterostructures AlGaAs/InGaAs/GaAs (P-HEMT), used for development of transistors for the millimeter wave band, was tested. The rate of etching of GaAs in typical mode was about 3 nm/min. The rate obtained is quite sufficient for preparation of gate grooves of field-effect transistors.

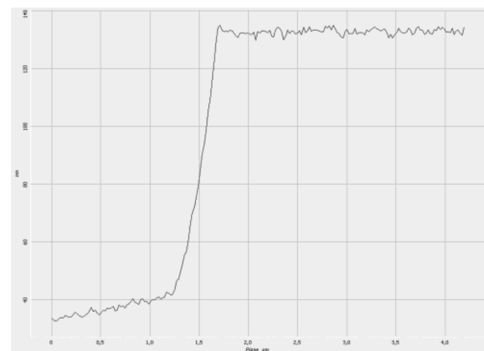


**Fig. 5** – Cross-sectional profile of etching zone border. Point value on horizontal axis is 0.5 $\mu$m, on vertical axis – 20 nm

The measurement of the characteristics of the two-dimensional electron gas did not reveal accumulation of radiation defects under the etching conditions pointed above. The slope of the etching area boundary measured with an atomic force microscope indicates to high anisotropy of the etching.

Further we apply this reactor for graphene production [4]. Most of presently available methods of graphene production apply mechanical exfoliation of graphite and also CVD deposition of graphene films. First of them ensures graphene flakes of the best structural perfection and the highest carrier mobility, but their lateral dimensions don't exceed tens microns. By the second method large graphene films (up to 10 inch) were produced but they have quite nonuniform structure and single crystal grains had dimensions not more than 100 nm. We have developed an alternative way of production of structurally perfect graphene samples by using soft, defectless etching of thin single crystals of natural graphite in the BPD reactor. The efficiency of this method is ensured by high quality and large area of graphite crystals and by soft, controllable character of such etching.

Blanks for producing graphene, that are single crystals with thickness of 30 – 100 nm and with lateral sizes up to 2 mm, are obtained by splitting thick single crystals by means of adhesive tape. Before splitting the crystals are attached to a optically transparent substrate with soluble adhesive layer. Substrate transparence lets checking uniformity of semi-transparent blanks after splitting. Then the adhesive layer is dissolved in organic solvent and remained thin crystal is thinned by etching in our reactor. Thickness of the crystal during the etching is monitored by measuring of its resistance in situ. The energy of ions is 60 – 80 eV while the resistance is < 100 Ohm and then is decreased to 20 eV thus providing soft flawless etching with a rate of about 0.2 nm/min at initial stage and 0.02 nm/min at final stage. The etching is terminated when the sheet resistance of the sample achieves ~ 1 kOhm that corresponding to 1 – 2 layer graphene.

Scanning of local Raman spectra with a spatial step of 0.2 $\mu$m shows the high quality of graphene films obtained and their high thickness uniformity within an area exceeding 1 mm$^2$.

Choice of the adhesive is very important for success of the process. At initial stage of the technique development [4] we applied an epoxy glue for the crystals attaching that provides a very thin and firm joining layer. However a strong bond of the layer with graphene leads to essential diminishing of carrier mobility and to free an graphene flake for transfer to other substrate turns out to be impossible. We have found out that poly(methyl methacrylate) (PMMA) which is widely used now for transfer of CVD-grown graphene films from transitional metals to convenient substrates is quite proper substance for our aim as well. Its solution in acetone after drying creates a rather firm adhesive layer which is removed easily from under a graphite crystal after its splitting or after graphene producing and its attaching to $SiO_2$/Si substrate.

A rather simple modification of the reactor mode transforms the reactor into a tool for deposition of carbonaceous films. For this aim a graphite disk is applied as the discharge collector, it is fed by the cathode voltage and a mixture of argon, hydrogen and methane is used as plasma creating medium.

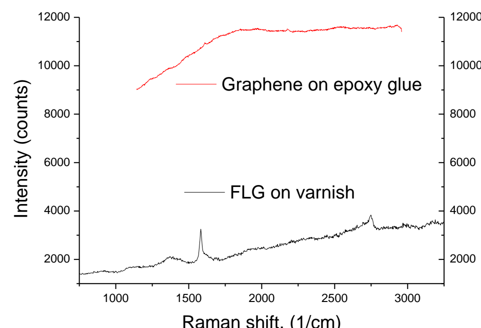
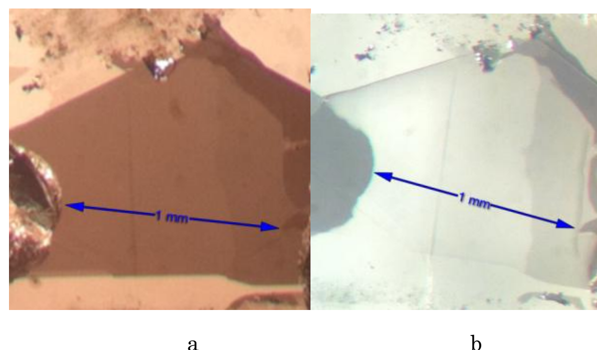



**Fig. 6** – Raman spectra of graphene samples attached with epoxy (top) and nitrocellulose varnish (low)




a b

Fig. 7 – A sample of graphene before etching (a) and after etching (b). Zones of different optical density are singlt-layer (left),bilayer (in centrum)graphenes and FLG (right).

Special tubular electrode coaxial to plasma column is applied to control the plasma potential relative to substrate. Thus the collector serves as a target sputtered with ions from the discharge accelerated up to 2 keV, and a substrate is exposed to bombardment of ions, molecules and radicals of C, H and CHx. In this way we receive diamond-like coating (DLC) with various electrical properties depending on plasma-substrate potential difference and gas components ratio [5]. However the most prospective application of this mode is deposition of graphene on epitaxial layer of transitional metal. Now we apply this technique for development of technology of single crystal graphene films on structurally perfect layer of nickel grown on a sapphire substrate.

## ACKNOWLEDGEMENTS

The report contains outcomes of researches that are fulfilled under funding by Russian Foundation for Basic Research (grants 07-08-00014, 11-08-00257) and by Ministry of Education and Science of Russia (Contract No 16.513.11.3066).

## REFERENCES

1. N.V. Isaev, A.I. Chmil', E.G. Shustin, *Plasma Phys. Rep.* **30**, 263 (2004)
2. E.G. Shustin, N.V. Isaev, M.P Temiryazeva, Yu.V. Fedorov, *Vacuum* **83**, 1350 (2009)
3. E.G. Shustin, N.V. Isaev, I.L. Klykov, V.V. Peskov, *Vacuum* **85**, 711 (2011)
4. Yu.I. Latyshev, A.P. Orlov, V.V. Peskov, *Doklady Physics* **57**, 3 (2012)
5. E.G. Shustin, N.V. Isaev, I.L. Klykov, *Tech. Phys.* **57**, (2012) (in press).