Beam plasma discharge in technologies of materials for nanoelectronics

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Abstract. The technologies developed at V.A. Kotel’nikov Institute of Radio Engineering and Electronics of RAS for specific application in nanoelectronics that are not used in industry are reviewed. Physical problems that were been solved at their development are analyzed, and found solutions are represented. Tested applications are briefly described.

1. Introduction. Historical review

Plasma processing reactors currently used in the production of semiconductor and quantum electronics devices provide various technological operations required for mass production of devices: surface cleaning, selective and anisotropic etching, implantation, deposition of films of dielectric and semiconductor materials. Tendencies to increase speed, memory and reduce the size of telecommunications systems, especially computers and military applications, require more and more attention to the technologies and tools that implement them.

This article provides an overview of the work carried out at the V.A. Kotel’nikov Institute of Radio Engineering and Electronics, Russian Academy of Sciences, on the development of new technologies of materials for nanoelectronics and photonics. Main part of this work uses a plasma processing reactor, in which a beam plasma discharge (BPD) is used as a plasma source.

The papers on the creation of plasmas for plasma processing reactors by an electron beam are well known (see for example [1] and cited there references). These systems are shown to be effective for the creation of plasmas with any gas composition and to be capable of creating high density plasmas with cold electrons ($T_e < 0.5$ eV). A beam of low density (1–10 mA.cm$^{-2}$), however, is used there, thus the “quiet” plasma is formed by collisional ionization by beam electrons with gas molecules. There are no intrinsic mechanisms of acceleration of ions or plasma in this system. A medium pressure is needed to obtain sufficient ionization, thus the ion flow is influenced by collisions and directivity of the ion flow is too low. Unlike this system, the beam plasma discharge (BPD), created at much greater beam density, is really a microwave discharge in fields generated in the plasma as a result of development of beam instability.

The formation of BPD, i.e. the creation of a plasma with a high concentration (significantly higher than that expected from collisions of beam electrons with gas molecules), when the beam propagated through a rarefied gas in a strong longitudinal magnetic field, was discovered in [2, 3] already at an early stage of experimental studies of beam plasma instabilities. The main manifestations of a beam-plasma discharge in a high magnetic field ($B^2/8\pi >> nT_e$) were: an abrupt increase in plasma density at a certain (threshold) value of the beam current, a significant increase in the diameter of the plasma column...
compared to the diameter of the electron beam, a clear high-frequency gain radiation from the plasma region and the transformation of its spectrum (from monochromatic or set of harmonics to a broadband spectrum in the $\omega_p$ band), a sharp increase in low frequency fluctuations.

A qualitative explanation of the observed phenomenon as a high frequency discharge in fields generated in the system as a result of the development of beam instability is given in [4–7]. At the same time, the ignition thresholds of the BPD in a high magnetic field, the oscillations spectra and the types of instabilities responsible for the formation and maintenance of the BPD, the energy relations in the BPD were experimentally studied [7–10].

The first work on the BPD theory appeared only in 1976 [11], and the development of the BPD theory was mainly determined by the desire to explain and describe the features observed in the BPD manifestations in active geophysical experiments and in laboratory experiments simulating their conditions (see for example [12]). Summing up the results of both theoretical and experimental works, we can construct the following qualitative picture of the formation and properties of the BPD.

At the initial stage of the discharge (after the injection of the electron beam into the gas medium is turned on), the gas is ionized due to collisions of the electron beam with molecules. If the ionization rate exceeds the rate of escape of charged particles from the ionization region, this “primary” plasma is accumulated. When a certain density of primary plasma accumulates in the system, beam instability should begin to develop on one of the proper types of waves in the plasma.

For a given set of experimental parameters, the ignition of the discharge occurs when the beam current exceeds a certain threshold value, which is associated with these parameters by an empirical dependence [12]:

$$I_i = \frac{E_0^{3/2}}{B_0} f(p),$$

where $f(p)$ is a function with minimum at $p = (1/2) \times 10^{-5}$ Torr for $E_0 = (1–3)$ keV, $B_0 \sim 40$ Gs, and varies about as $p^{\beta}$ ($0.5 < \beta < 1$) up and down this pressure.

The rate of ionization of neutral atoms during the ignition of the BPD increases by 2 orders of magnitude compared with the speed of collisional ionization by a beam under the same conditions. Since the diffusion rate also increases with the plasma temperature, the plasma density in the discharge increases by a smaller value.

Starting from 1972–1974, experimental studies of BPD began at several laboratories to study the prospects for its applications in plasma chemistry. This idea attracted attention of researchers in connection with the problems of non-equilibrium plasma chemistry: since the temperatures of ions and electrons at the beam-plasma discharge differ essentially even at the highest pressures of the working environment. Thus chemical reactions and the production of materials, which are impossible in ordinary, equilibrium chemistry, are possible. These works did not receive wide distribution primarily because of the low productivity of such processes (the maximum working pressure of the medium in which the discharge was ignited was several Torr). Now this direction of R&D gets new continuation due to works of Tomsk team of researchers (see, for example [13]).

2. Our experiments

Our researches on application of BPD for plasma processing technologies began in the 1997. Then we began studies of the ion component properties at the beam plasma discharge. A scheme of experimental installation is shown on figure 1a.

We revealed that BPD in a low gas pressure can serve as a source of ions in range of 10–100 eV [14, 15]. These ions propagates from the core of the discharge to its periphery normally to the discharge axis. Their energies substantially exceed the electron thermal energy and can exceed the energy acquired by the ions in the electrostatic field between the discharge plasma column and the chamber wall. Changing the external parameters of a BPD in the equipotential interaction chamber and using controlling electron beams in velocity, the energy of the ions acting on the surface of a sample placed near the side wall of the chamber can be varied within a range of 10–70 eV (figure 2a). This ion energy range is characteristic
for plasma-processing reactors for surface treatment, such as deposition of thin films and etching, of materials for semiconductor electronics and acoustoelectronics.

**Figure 1.** The experiment schematic (a) and image of the BPD reactor (b).

In order to give a clearer insight into the ion acceleration mechanism, we carried out computer simulation [16] of the interactions in a beam–plasma system for model parameters that correspond qualitatively to those of the experiments performed in [2].

Our simulations were carried out with the KARAT code [17–19]. The mathematical model underlying the code is based on Maxwell’s equations supplemented with various constitutive equations (in particular, kinetic equation solved by a particle-in-cell (PIC) method) and phenomenological model equations. Maxwell’s equations were integrated explicitly by a finite difference scheme of second-order accuracy on staggered grids.

This first simulation was carried out with rather simplified model: we used a two-dimensional axisymmetric version of the KARAT code in which all the components of the particle velocities are taken into account. Ionization was ignored. A particle beam with energy of 2 keV and current of 0.5 A was injected into the cylinder through an inlet of radius 1 cm. The cylinder was initially filled with plasma of density $10^{10}$ cm$^{-3}$ and was placed in an external steady magnetic field with induction of 50 G.

The main results of the calculations can be seen on figure 3. During the nonlinear development of beam instability within a finite volume (plasma-filled cavity), in the region occupied by the electron beam a strongly non-equilibrium plasma is produced with a very hot anisotropic electron component (the mean energy can amount to a few hundred electron-volts), so the distribution functions of the beam.
and plasma electrons become physically indistinguishable. The instability that develops in the system results in the formation of two plasma regions with different parameters. First, this is the beam region, where intense stochastic oscillations at frequencies close to the Langmuir frequency are localized. The second region is at the periphery, where the excited waves are far less intense and do not have any substantial influence on the plasma parameters there. The electrons in the first region drive an additional electron current from the plasma to the end electrodes. An increase in the electron current leads to the growth of the plasma potential in the beam region. The potential gradient between the beam region and the peripheral plasma region accelerates ions along a normal to the axis of the system. Because of significant electron fluxes from the axial region toward the ends of the system, the potential in this region increases, so un-magnetized ions begin to drift from the axial region toward the periphery. The energy of the ions so accelerated can be as high as several tens of electron-volts.

**Figure 3.** Phase portraits of the beam electrons at $t = (a) 6, (b) 8, (c) 10$, and (d) 120 ns.

Different methods exist of controlling the distribution function of ions acting on a conducting structure on an insulating substrate. Way, which is well known and widely used in industry, comprises in varying the high-frequency sinusoidal voltage bias on the substrate electrode. This way results in a typically broad, often bimodal form of the ion distribution function on energies (IDF) (see, for example, the review [20] and articles cited there). The shape of the IDF curve on the substrate surface is shown to significantly affect chemical reactions on a processed surface.

For plasma reactor based on beam plasma discharge (BPDR) two methods were proposed of controlling the distribution function of the ions [21]. In the first case, a periodic pulsed voltage was applied to the substrate holder; in the second case, the pulsed voltage was applied to the beam collector, thus modulating the plasma potential. We tested these techniques experimentally and by computer simulation to investigate space distributions of the BPD plasma density and the ion flux energy to the side electrode, imitating a substrate holder of plasma processing reactor (see figure 2). The comparison showed that the second method provided a more efficient control of the distribution function of the ions, acting on the treated substrate. Further we used a combination of both ways to treat several samples on different holders with different ion energies.

Thus we designed and created a novel plasma processing reactor for treatment of materials used in electronics engineering (figure 1b) [22].
3. Applications: Etching
First application of this reactor was soft etching technology of AlGaAs barrier layers in semiconducting AlGaAs/InGaAs/GaAs heterostructures, exploitable for design of microwave field transistors [15]. Analysis of etched samples was performed using an atomic force microscope (AFM) and by measurement of the concentration and mobility of a two-dimensional electron gas, sensitive to radiation defects. The rate of etching of GaAs got 3 nm min⁻¹ Ion mean energy 60 eV. Because low energy etching is required mainly for preparation of gate grooves of field-effect transistors, and the depth of etching should not exceed 10–20 nm, the rate obtained is quite sufficient for industrial application of the method.

The measurement of the characteristics of the two-dimensional electron gas did not reveal accumulation of radiation defects under the used etch conditions. There was no detected indications of non-uniformity of etching on patterns of 60 mm in diameter. The slope of the etching area boundary did not differ from a slope of the boundary of a mask that indicated the high anisotropy of the ion flow (see figure 4). Thus the BPD reactor found possible application for a "soft" defect-free etching of a surface available for nanoelectronics technology.

We proposed and tested the BPD reactor for fabrication technology of monatomic graphite layers (graphene) and other conductive layered materials [23]. Thin graphite crystals of thickness from ten to hundreds of atomic layers with lateral sizes about 0.5 mm, being workpieces for subsequent etching, were produced by thinning natural graphite single crystals glued on saphire or glass substrates using an adhesive tape. Such a method made it possible to obtain thinner initial graphite crystals. After adhesive tape dissolution in acetone, the remaining thin graphite crystal flake was transferred onto a proper substrate. Then, indium electrodes were applied to sample boundaries, and the crystal was thinned by plasma etching in the BPD reactor in an argon atmosphere. The film thickness was measured in situ by the resistance in the plasma reactor chamber. The resistance time behavior made it possible to estimate the etch rate and to determine its end time point: the resistance of a square of a homogeneous monolayer is estimated as ~2–3 kΩ. The argon ion energy was 50 eV at the initial etching stage and decreased to 20 eV at the final stage, when the inter-electrode resistance reached ~100 Ω, thus minimizing the probability of introducing radiation defects.

Graphite films fabricated with such a way were characterized by Raman spectroscopy. A typical spectrum is shown in figure 5. The ratio of G- and 2D-peaks amplitudes corresponds to bilayer graphene. The G-peak narrowness indicates the high structural quality of the sample. Homogeneity of the obtained graphene films over the sample area were proved. Thus samples of structurally perfect bilayer graphene with characteristic sizes exceeding 100×100 μm² and few layered graphene (FLG) samples with characteristic sizes exceeding 500×500 μm² were fabricated then for the first time.
So, the new techniques of fabrication of atomic-thin films from natural layered materials with relatively large lateral sizes was demonstrated.

4. Applications: Carbon films deposition

We applied our reactor for deposition of carbon films by PECVD techniques [24]. For this aim we modified its scheme and regimes: the discharge collector was made from graphite and fed with a voltage of the cathode. The plasma potential was controlled with the additional electrode, which was a short tube, set near the chamber inlet coaxially to the electron beam. Thus carbon atoms and ions were produced by sputtering the collector material, and energy of ions C and Ar was controlled by the way of varying the modulating electrode voltage. This technique differs from usual schemes of PECVD synthesis of DLC films by the way of cracking hydrocarbon gases in gas discharge, providing more simple control of energy of an ion flow and also more uniform composition of atoms and ions acting to the sustracte. The samples of nanosized DLC films thus produced at various energies of ions acting onto deposited film had different electro-physical properties depending on this energy. The best films on resistance and the breakdown voltage were obtained at mean ion energy 100 eV (see figure 6).

Figure 5. Local Raman spectrum of the graphite sample after etching [23].

Figure 6. Volt-ampere characteristics of the samples of DLC films deposited at various pulse voltages at the modulating electrode: \( V_{mod} = 30 \text{ V (1); 50 V (2); 70 V (3); 100 V (4) [24]}. \)
The method of charge relaxation spectroscopy (Q-DLTS) revealed the effect of adsorbed water vapor and alcohol on the electrical properties of the films, which indicates the possibility of using the obtained films as an active adsorbing material for chemical sensors.

5. Applications: Patterning of microstructures

Now interest has been growing in developing nanoelectronic devices including “microwire on isolator” types of structure (see for example [25–27]). For example, patterning graphene into a nanoribbon can open a bandgap that can be tuned by changing the ribbon width, imparting desired properties.

The successful use of technology for producing defect-free nanoscale films with in situ control of their thickness stimulated the proposal to obtain in this way two-dimensional structures that are promising for use in nanoelectronics and spintronics. Thus, work was started on obtaining nanoribbons of an topological insulator by etching pristine single crystals of this material, similar to the method by which samples of two-layer graphene [19] were obtained. These experiments gave a mixed result: the desired etching effect was observed for ions with energy $\geq 70$ eV acting on the initial strips but the resulting structures were found to be highly heterogeneous in thickness (because of this relatively disappointing result, information about these experiments was not published). There was a natural assumption that the unevenness was caused by the inhomogeneity of the ion flow, and it may be possible to exclude or weaken the negative charging effect on the dielectric by means of pulse modulation of the conductor potential. Thus, we started computer modeling of the etching process when conductors on a dielectric substrate are subject to plasma treatment [28–30].

To study the processes with a pulsed potential on a conductor, it was necessary to use a model that eliminates the effects of plasma depletion and keeps the main plasma parameters constant in an area sufficiently remote from the conductor. We investigate the action of ion flows from a plasma onto the surface of a microwire, which is a flat conductor lying on an insulator, with width less than the plasma Debye length. The goal of that work was to study the effects of charging a dielectric surface in a complex configuration consisting of a microwire supported on an insulating substrate in [28]. A limitation of this approach was that we could observe only transient processes when a potential was applied to the microwire: the analysis time was limited by the depletion of the plasma because of the arrival and neutralization of charges at the wall. Nevertheless, the main qualitative effect of charging was clearly shown: the formation of an electrostatic lens, leading to a substantial inhomogeneity in the profile of the ion beam acting on the microwire (see figure 7).

![Figure 7](image-url)

**Figure 7.** Geometry of the simulated system (a) and the distribution of argon ions in the (X, Z) plane at a constant electrode potential of 70 V.
Then the model was constructed allowing computer simulations of the near-wall area of a planar plasma sheet in conditions where the steady state of the plasma is supported by the production of charged particles in a region removed from the wall [29]. Calculations have revealed variation in the energy distribution of the electrons in both time and spatially over the sheet width (cooling the electronic component) due to absorption of fast electrons at the walls bounding the plasma volume. It is shown that the plasma density profile across the sheet width has an abrupt decrease at the boundary of the region of plasma regulation. Let’s recall that the standard concept of the potential and plasma density distributions in the sheath and presheath is based on the assumption of a stable energy distribution for the electrons in the presheath. Thus it was shown, that this concept yields inaccurate results for the plasma sheet where the ionization source is remote from the wall.

At last, a model has been designed to allow investigation of dynamics of the plasma adjacent to the microwire, either with a steady state potential applied to the microwire, or under the action of periodic pulses. It was revealed that more complex pulse shapes than rectangle one can provide a very much more homogeneous distribution of the etching rate (at the 10% level) over the microwire surface (see figure 8 [30]).

![Figure 8](image)

**Figure 8.** The sputtering rate vs. the position across the conductor on the electrode (b) for various shapes of the conductor potential in time (a). 1 – DC bias on the conductor; 2 – rectangular voltage pulses; 3 – trapezoidal voltage pulses.

Seeking the optimal form of the signal modulating the plasma potential for uniform etching structures of “microwire on isolator” kind is being performed further.

6. Conclusion. What is further?
The plasma processes are being actively developed for the nanoelectronic applications. Multiple research groups are involved in the study, and industrial equipment for nanoelectronic technologies is available. Evidently, the corresponding problems can be solved using both improvement of the known processes and schemes and application of qualitatively new approaches. Some of them employ sources of electron, ion and neutral beams both for the creating plasmas with specific properties and for etching structures in the absence or diminishing of surface charging and structural damages caused by UV and particle radiation. New materials, in particular, GaAs and GaN, CNTs, graphene, organic semiconductors, and biosupermolecules are actively studied and employed in nanoelectronics. This circumstance necessitates the development of atomic-layer processes with ultimately low concentrations of defects and accurate control of reacting components and their energies. We (I and my collaborators) believe that the processes with pulsed electron beams for plasmas creation are promising tools for the atomic-layer defect-free etching, and are going to work in this direction. Future nanosized devices will be fabricated at relatively low etching rates, so that neutral-beam etching is a promising method that provides desired characteristics of nanomaterials and nanostructures, and probably an electron beam excited plasma with rather low electron temperature will be the most proper medium for producing such
beams in spite of low efficiency of their producing. In our opinion, both pulse-modulated plasma and neutral beams are promising candidates for the defect-free etching in the fabrication of nanosized devices.

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