Recent Advances in Surface Processing at NPI (Equipment and Methods)

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Abstract – The review is devoted to the analysis of the present state-of-the-art and development trends of the new methods and equipment being developed in the Nuclear Physics Institute, Tomsk (NPI), for dc vacuum arc-based ion and plasma materials processing. The features and advantages are demonstrated for the method of high-concentration implantation with compensation of surface ion sputtering by metal plasma deposition, the method of metal plasma deposition under repetitively – pulsed ion mixing with ion beams and plasma flow formed in the "Raduga-5" source, and the method of coating deposition and ion implantation, including an application of the filtered dc metal plasma source and high-frequency short-pulsed negative bias voltage with a duty factor in the range 10–99 %. The features of ion implantation and metal plasma deposition for dielectric, semi-conducting and metal samples are presented.

1. Introduction

In order to improve performance characteristics of metallic details and units, significant concentrations and doses of embedded atoms are necessary. This requires the development of high-productivity and, at the same time, simple and reliable equipment realizing novel methods of ion processing.

The development of equipment and methods providing a wide spectrum of high-productivity technological regimes for implantation in conducting materials, in which a high concentration of embedded atoms (up to 100 at.%) at a sample's surface can be achieved, is anticipated. Such concentrations are necessary to obtain good adhesion properties of deposited coatings. It also seems crucially important to develop methods providing simple and reliable modes of ion implantation into dielectrics and ion assisted metal plasma deposition, which are applicable equally to conducting or dielectric samples.

In this paper, the complex of ion and plasma processing methods developed at NPI is described. It is based on the usage of vacuum arc microparticle-filtered metal plasma and repetitively-pulsed formation of ion beams and streams from this plasma, making possible different modes of ion implantation and ion assistance for metal plasma deposition.

2. Repetitively-pulsed ion beam assisted metal plasma deposition

The method of ion beam assisted deposition (IBAD), widely investigated in recent years, is a unique instrument for the formation of high-quality coatings with excellent adhesion properties [1–5]. The ion beam and plasma sources developed at NPI allow a wide range of opportunities for metal plasma ion beam assisted deposition technological regimes [6–8]. First of all, it should be noted that at a fixed current of vacuum arc discharge and, correspondingly, a fixed concentration of obtained plasma, the average current of the ion beam can be easily controlled over a wide range by changing the pulse repetition rate. Fig. 1 presents a result of average ion beam current and plasma ion saturation current measurements depending on distance from the output of ion beam and plasma source "Raduga-5" [8].

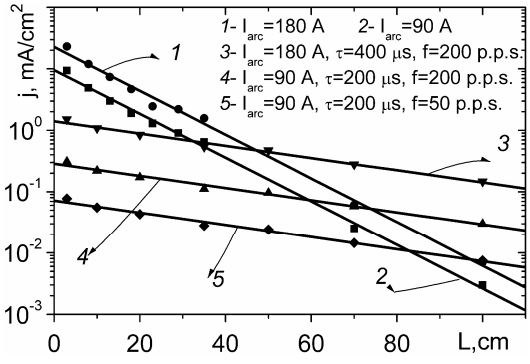

Fig. 1. Ion average current density ($j_{av}=j_p f\tau$) (3–5) and plasma ion saturation current density (1, 2) at various distances from the sources

The relation between the average ion beam density and plasma ion saturation current density at the sample can be changed by variation of the distance from the "Raduga-5" source. Let us consider in more detail the situation directly at the output of "Raduga-5" source. The average ion saturation current density of the plasma stream to the target in the case of "Raduga-5" is determined by the expression:

$$J_p = \sum_{i=1}^{k} Z_i e n_{0i} v_i (1 - f\tau), \quad (1)$$

where f – pulse repetition rate of the ion beams, τ – pulse duration, Z_i – ion charge state, n_{0i} – plasma concentration, and v_i – velocity of the plasma stream.

The ion beam density at the same sample is determined by the expression:

$$J_p = \sum_{i=1}^{k} Z_i e n_i f\tau (2Z_i eU / M)^{1/2}, \quad (2)$$

where: n_i – ion beam concentration, U – accelerating voltage, and M – ion mass.

Taking into account Eqs. (1) and (2), one can determine the relation between plasma ion saturation current density and average ion beam density at the sample as :

$$J_p / J_b = (1/ f\tau - 1). \quad (3)$$

At maximum pulse repetition rate f=200 p.p.s., and τ=400 s, $f\tau = 8 \cdot 10^{-2}$, and J_p/J_b=12.5. So, at the output of the "Raduga-5" ion beam and plasma source, the flux of plasma ions to the sample at maximum average ion beam density is only 12.5 times greater than the flux of accelerated ions. At the same time we have to take into account that the IBAD process is followed by ion beam sputtering of the coatings under deposition. Assuming the coefficient of ion sputtering of a Ti coating surface (titanium ions with 110 keV energy) to be ~3 atoms per ion, one can calculate that the relation is reduced down to the magnitude of about 4.2. Assuming also that the density of the coating deposited corresponds to titanium density, and the projected range of 110 keV titanium ions is approximately 10^3, one can estimate the dose of dynamic ion mixing affecting the coating-sample intermediate layer when the thickness of the coating is increased from 0 up to 10^3. This ion implantation dose can be estimated as higher than 10^{17} ion/cm^2. So, the maximum average current density of accelerated ions even at the "Raduga-5" output is sufficient for effective ion mixing of the intermediate layer between the coating and the sample.

As the distance from the source increases, the plasma density decreases much more rapidly than the ion beam density. Subsequently the effective regimes of IBAD, in this case, can be obtained for low ion beam pulse repetition rate.

On the other hand, for high ion beam pulse repetition rate, at a distance from output of "Raduga-5", the regime of high concentration ion implantation (HCII) can be realized.

3. High concentration ion implantation (HCII)

One of the limitations of the potential of the method of ion implantation is connected with ion sputtering of the surface layer during the process of ion beam bombardment. By reducing the sputtering coefficient S or fully eliminating the effect of surface sputtering at ion implantation, one can increase, correspondingly, by S times (at full elimination of sputtering) the maximum achievable concentration and maximum dose of implanted impurity.

This task becomes especially important for the development of the methods of ion beam modification of metals and alloys. High irradiation doses (10^{17}–10^{18} cm^{-2}) result in significant surface layer sputtering – its depth sometimes exceeds the range of accelerated ions in a material by tens and even hundreds of times.

The essence of the HCII method is in compensation for ion sputtering of the implanted target surface by deposition of a metal plasma [9, 10, 11].

During the process of ion implantation, including repetitively-pulsed processes, gradual sputtering of the material surface layer occurs together with the accumulation of dopants in a sample. After irradiation of the target by the ion beam with the dose D_{ir}, the thickness of sputtered layer d can be estimated as:

$$d = SD_{ir}/N_0. \quad (4)$$

If after that, one deposits plasma on to the target surface until recovering its initial boundary, so that the next irradiation of the target by ions with the dose D_{ir} would lead only to sputtering of this skin film. Consequently, in this way, the conditions of a pulsed implantation process may be repeated (not accounting for sputtering anomalies caused by film presence). The dopant concentration will increase continuously. The effect of concentration increasing is significant if the thickness of the material sputtered under accelerated ions for one implantation cycle does not exceed R_p, i.e., if the peak of concentration profile is not at the substance surface, but rather at a certain depth. The smaller the thickness of material sputtered for one implantation cycle, the higher the dopant concentration achieved in the material.

Regarding the source of ions and plasma, the mode of high concentration implantation requires, in the first iteration, that the following condition is satisfied:

$$S = (\tau_p - \tau_u)/\tau_u. \quad (5)$$

However, this formula requires correction for the actual experimental conditions. First, if the target is located at some distance L from the source, one should take into account that the current density of the ion beam and the plasma density decrease depending on the distance, following different laws. The beam current density decrease depends on its angular divergence and can be insignificant, whereas the plasma density, in the absence of a guiding magnetic field, decreases approximately as $1/L^2$. So, if the target is placed further from the source, the relation (5) should be increased. In the case of metal plasma-immersion ion implantation, when the ion-emitting boundary practically touches the processed detail surface, the expression (5) does not require correction.

It should, nevertheless, be taken into consideration that at the formation of plasma in the source, the extent of ionization of the operating substance is high (>90 %) only for refractory materials. In most cases, along with the plasma generation in the source, the flow of neutral atoms is created, that also can be used for deposition onto the target and compensation of sputtering. Introducing the correcting coefficient Q accounting for irradiation geometry, efficiency of ion beam extraction from plasma flow, attachment factors, and the presence of the neutral component, one can write the condition for achieving the high concentration implantation mode as follows:

$$QS=(\tau_p/\tau_u-1). \quad (6)$$

The value of Q in the experiment is determined from the film deposition rate with no accelerating voltage in the source.

As a result of the introduction of implanted material atoms from the surface into the target as recoil atoms, the accumulated dose of dopant can exceed the irradiation dose, whereas the near surface concentration can reach 100 at.%. The curves presented in Fig. 2 characterize the change in Ti target irradiation dose (D_{ir}) with Al ions and the integral dose of Al interstitial atoms (D_{in}) as functions of ion treatment time. As follows from the presented data, the ratio $D_{in}/D_{ir}>1$ is characteristic for all time intervals of ion treatment. The observed increase in intensity of dopant storage with increase in treatment time is apparently connected with implantation and mixing of the already formed modified layer. The example of the Ti→Ni system formation (curves 3 and 4) shows that in the case of increase in the plasma stream density, the intensity of dopant accumulation increases. In this connection, the observed film growth on the target surface does not significantly influence the dynamics of dopant accumulation.

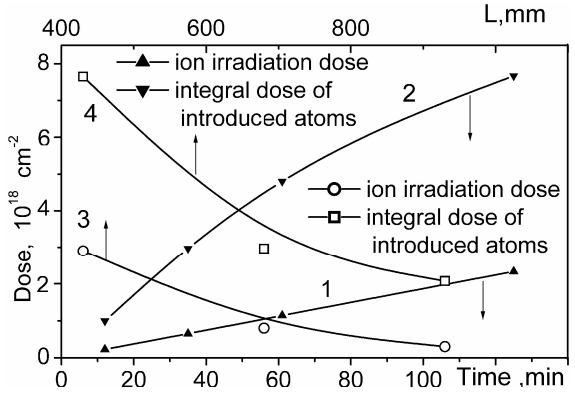

Fig. 2. Change in irradiation dose and integral dose of introduced dopant depending on: 1,2 – ion implantation time (Al→Ti system, L=0,4 m); 3,4 – distance to the ion source output (Ti→Ni system)

It is important to note that in the mode of high concentration implantation, the rate of dopant storage under high irradiation doses increases more than S times. The dose of introduced atoms is enabled to exceed the irradiation dose due to the embedding of recoil atoms from the film into the surface, if ion sputtering is compensated by deposition of plasma whose composition is the same as that of the ion beam.

Taking into account that in some cases, the sputtering coefficient S can be significant, the time and cost of ion beam material processing are reduced correspondingly.

4. High frequency metal plasma immersion ion implantation or deposition

The method of high frequency short-pulsed plasma immersion ion implantation or deposition (HFSPPI^{3}D) can be used either by itself or to extend the range of technological possibilities of installations containing the sources of "Raduga-5" type, including those with additional vacuum arc plasma generators with plasma filters.

The HFSPPI^{3}D method [12, 13] has a number of advantages in comparison with the usual approach to realization of metal plasma immersion ion implantation and deposition (MPI^{3}D) [14–16].

Using a metal plasma formed by the vacuum arc plasma generator operating in the dc mode satisfies the prerequisites for high productivity of a technological process. Taking into account the necessity of short pulse bias voltage formation (this is an obligatory condition for dielectric treatment), the relation between plasma ion saturation current density and average ion beam density can be changed only by increasing the pulse repetition rate. In accordance with Eqs. (3) at bias potential pulse duration about microsecond order the pulse repetition rate should constitute hundreds of kHz. A short pulse duration τ and high repetition rate f of negative bias potentials applied to samples, where $f\tau$=(10–99 %) allow for using this method in ion assisted metal plasma deposition, high concentration metal ion implantation, and for realization of practically "pure" ion implantation.

Application of the Raduga-5 source along with HFSPI^{3}D allows one to provide preliminary cleaning of samples and their heating using only a metal plasma. HFSPPI^{3}D promotes the increase of atom penetration depth for implantation with the Raduga-5 source, due to additional intensive ion processing of the surface and surface heating, up to practically any temperature.

Another principal feature of the HFSPPI^{3}D method lies in the fact that it makes possible implantation of metal ions and deposition of strong-adhesion coatings in the case of dielectric samples.

Formation of ions accelerated from the plasma near dielectric samples takes place in the double layer of charge separation due to displacement currents conditioned by the presence of capacitance, which is formed by the electrode for applying bias potential,

the dielectric itself, and the plasma adjoining the dielectric.

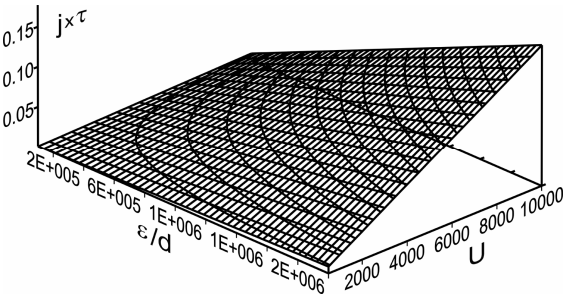

Fig. 3. Plot showing application parameter space for dielectric materials

Fig. 3 demonstrates the application of the HFSPI³D method as applied to dielectric materials. The region where this method is effective lies under the surface, being determined by the characteristics of the dielectric (through the relation of dielectric permittivity and thickness of the sample), by the bias voltage amplitude and by the product of ion current density from plasma and the pulse duration. The figure indicates that a high-density plasma providing ion current density of the order of hundreds of A/cm^2 can be used for modification of the properties of dielectric targets with a bias voltage pulse duration about tens or hundreds of nanoseconds. It also shows the performance of low-density plasma providing ion current density of the order of tens or hundreds of μA/cm^2, where pulse duration can be increased up to tens or hundreds of microseconds without decrease of efficiency.

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