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Present status and prospects of research in SINS on the modification of surface properties by pulsed plasma streams

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Abstract The paper presents examples of the most important results obtained in SINS during the last decade, interesting from the point of view of industrial applications. It also indicates some of the most prospective directions in research on modification of the surface properties of materials by means of pulsed plasma streams.

Key words IONOTRON plasma injector • pulsed plasma processing • surface modification

Introduction

The first successful experiments on the modification of surface properties of materials by means of high-intensity pulsed ion beams were carried out at the beginning of the eighties. The feasibility of a post-implantation silicon annealing as well as the formation of silicides, as a result of a treatment with high intensity pulsed proton beams generated in magnetically insulated high voltage diodes, was demonstrated at Cornell University [1]. In 1981, the feasibility of p-n junctions forming in monocrystalline silicon for photovoltaic cell production purposes, with high intensity pulsed BF_3 plasma streams, was shown firstly in SINS [7].

The main parameter of the pulsed processing of a solid surface is a power delivered to the treated surface. The pulsed ion or plasma beams with a power flux of the order of MW/cm^2 can melt a near-surface region, and simultaneously can dope the melted layer. To avoid damages caused by violent boiling and mass ablation of the substrate the power flux incident on the surface has to be limited to about 10^7 W/cm^2. It is also known that for the substantial modification of semiconductors the doses of the order of 10^{14}–10^{15} cm^{-2} are needed. In the case of metals and ceramics the required doses attain a level of 10^{16}–10^{17} cm^{-2}. In high-voltage ion diodes (typically 10^{-7} s pulse duration, 200–400 keV ion energy) the doses can reach maximum 10^{14} cm^{-2}. One can notice that for the modification of metals with high energy ion beams only purely thermal effects (caused by rapid cooling, 10^7–10^{11} K/s) or effects associated with fast heating and ablation (shock waves) can be utilized. The intense plasma pulses (of the order of microsecond pulse duration, 1–10 keV ion energy range, 1–10 J/cm^2 energy density) introduce doses, which may reach values above 10^3 times higher per pulse.

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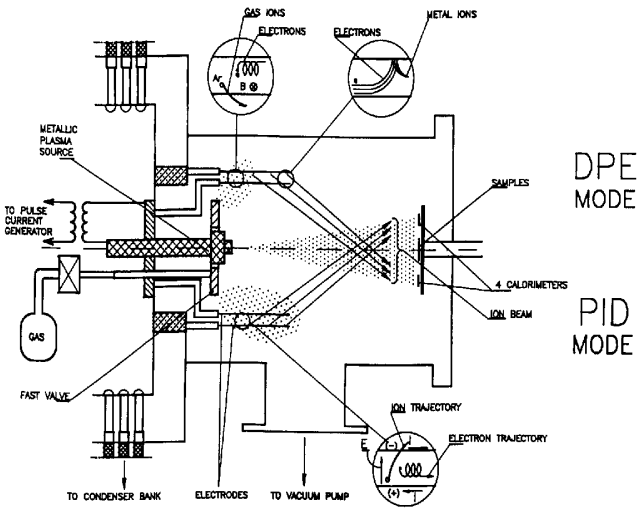

Fig. 1. Schematic diagram of the IONOTRON device.

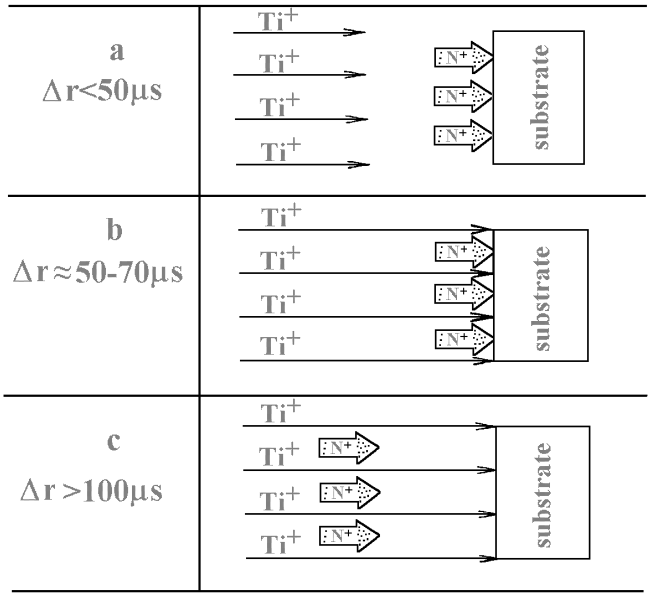

Fig. 2. Various versions of the deposition conditions.

Nevertheless, it was shown by Shulov et al. [16] that the beams generated in the high voltage diodes can be successfully applied for industrial purposes.

Except the IPD deposition method [17], high-intensity pulsed plasma streams did not find wide industrial applications till the present time, but recently one can observe a growing interest in such a method of the modification of various materials.

Apparatus

The high intensity plasma pulses are produced in the IONOTRON – plasma injector, which is a special plasma accelerator, originally developed in IPJ for thermonuclear fusion purposes and subsequently modified for applications in material processing. This accelerator was described elsewhere [3], but for the sake of completeness the most important characteristics of this device should be presented below.

In the IONOTRON, schematically presented in Fig. 1, plasma pulses are produced by low-pressure electric discharges initiated between two cylindrical, transparent for particles, electrodes. Discharge energy from a capacitive storage bank is applied when the working gas in the inter-electrode space attains the required density. The working gas is injected through a fast gas-valve located on the axis of the electrodes. Depending on gas conditions two operating modes are possible. The first is the pulse implantation doping (PID) mode, and the second is the deposition by pulsed erosion (DPE) mode. In the PID mode, the discharge produces a high intensity (up to 100 kA), short-duration (about 1 μs) plasma pulse, containing exclusively the ions of the working gas. The energy flux density of the plasma streams is in the range of 1–10 J/cm^2. In the DPE mode, an arc erosion of the electrodes takes place, and the ions and neutrals of the electrode material are present in the plasma. The results of our recent investigations on kinetics of the pulsed erosion deposition process [6] indicate that low-energy metallic ions reach the surface, when it is already solidified after being first melted by the working gas plasma. The metallic coating is molten and mixed into the substrate during the subsequent pulse.

In the experiments conducted so far the diameters of outer and inner electrodes were 130 and 90 mm, respectively. The high-voltage pulse applied to the electrodes was supplied from the capacitive storage bank of 15 to 60 kJ. At a distance of 20 to 30 cm from the ends of the electrodes there was obtained 20% uniformity of the plasma streams. The energy spectrum of the ions is continuous, while the mean energy of the ions varies from several hundreds of eV to several tens of keV depending on the operation conditions. For the extension of possibilities of the IONOTRON additional pulsed or DC metallic plasma sources, based on the metal vapour vacuum-arc concept, were also installed in the vacuum chamber of the accelerator.

In the first case, a high-current pulsed metallic plasma source is located inside the electrode space, on the axis of the IONOTRON. The appropriate synchronization between the discharge ignition and the metallic source action, makes it possible to accomplish the process in which the stream of a metallic plasma impinges on the melted surface of the processed material. The three various situations for N^+ and Ti^+ ions, presented schematically in Fig. 2, can be realized by a change of the delay time $\Delta\tau$ between triggering of the metallic plasma source and the main discharge ignition. The time of flight of metallic ions from the source to the substrate surface amounts to about 50 μs. In the case (a) at $\Delta\tau < 50$ μs, the nitrogen ions reach the substrate first and heat the surface, (b) at $\Delta\tau = 50$–70 μs and both nitrogen and metal ions reach the substrate simultaneously, (c) at $\Delta\tau > 100$ μs the metal ions arrive first, resulting in the predeposition of a metallic film, before nitrogen ions start to heat the surface.

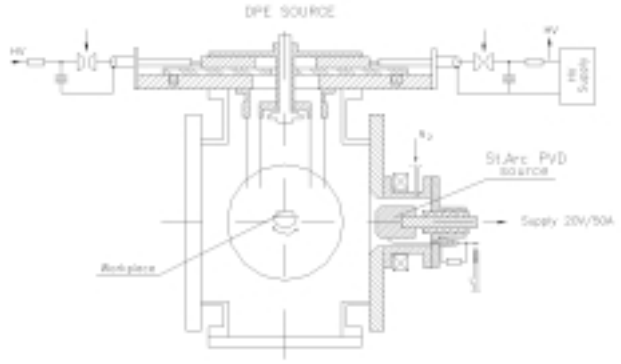

Fig. 3. Schematic diagram of the combined DPE and PVD processing.

A steered arc-plasma source, with a DC supply system (20 V/50 A), was installed perpendicularly to the IONOTRON axis, as shown in Fig. 3. In this case, the samples located on a revolving holder were firstly treated with a pulsed plasma stream and subsequently, after a turn they were coated with the use a conventional PVD method. During this processing the samples were heated and biased.

Pulsed plasma processing

A significant part of our studies on the modification of surface properties of various materials with pulsed plasma streams, was focused on the formation of n^+-p-p^+ and p^+-n-n^+ photovoltaic structures in mono- and poly-crystalline silicon [7, 11, 14]. For this purpose, BF_3 was used as a working gas, providing boron dopant to obtain p^+ layers in n-type Si, while PF_5 (phosphorus source) was used to form n^+ contact. The mean photovoltaic conversion efficiency obtained for a set of 100 solar cells, formed on the monocrystalline silicone, was 13.5%, as compared to a value of 14–15% typical for silicon solar cells mass-produced using a

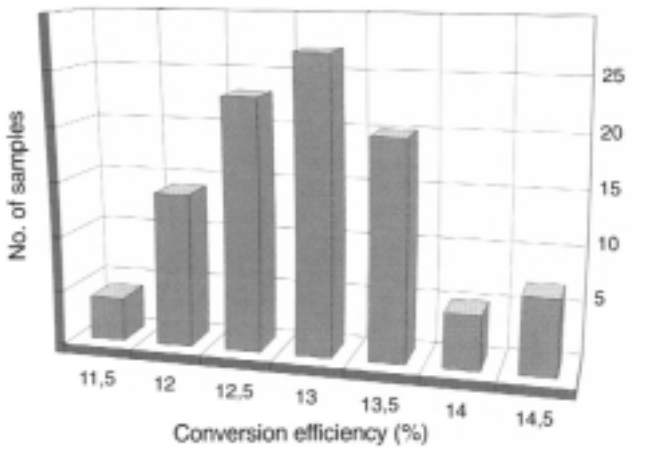

Fig. 4. A histogram of the efficiency of a set of 100 Si solar-cells manufactured using the PID method.

conventional diffusion process. A histogram of the cell efficiency obtained for a set of 100 solar cells, as presented in Fig. 4, demonstrates both, good reproducibility, and planar uniformity of the process, which after some refinements may appear competitive to ion implantation techniques of the mass production of solar cells.

A significant part of our effort was devoted to a study of steels doping with nitrogen plasma pulses [8, 9, 13]. It was shown that high doses of nitrogen (of the order of 10^{17} cm^{-2}) can be introduced into steel by using nitrogen plasma pulses with an energy flux density of 5–10 J/cm^2. Typical profiles of the retained nitrogen in the 18/8 stainless steel after 5 and 10 plasma pulses, as deduced from the ^{14}N (d,α)^{12}C nuclear-reaction analysis, are shown in Fig. 5. Such profiles can be fitted with expressions derived from a diffusion model, assuming a constant diffusion coefficient of nitrogen in the molten steel, and a diffusion time corresponding to the total time of the molten phase. The retained nitrogen concentrations are close to, or even exceed, the limit achievable after

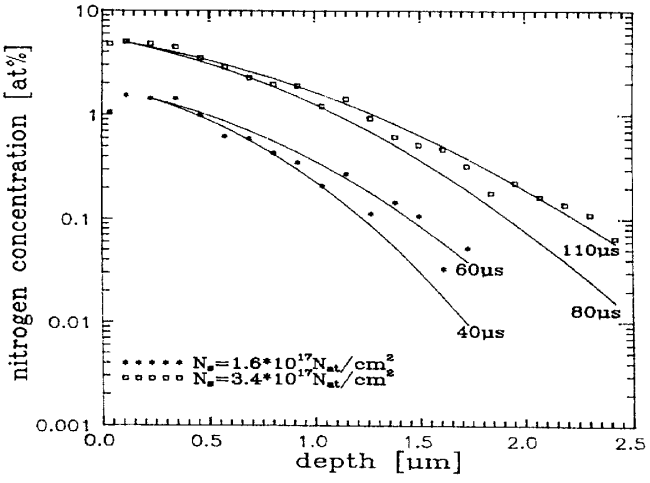

Fig. 5. Typical profiles of retained nitrogen in the 18/8 stainless steel after 5 and 10 nitrogen plasma pulses, as deduced from the ^{14}N (d,α)^{12}C nuclear reaction analysis [13].

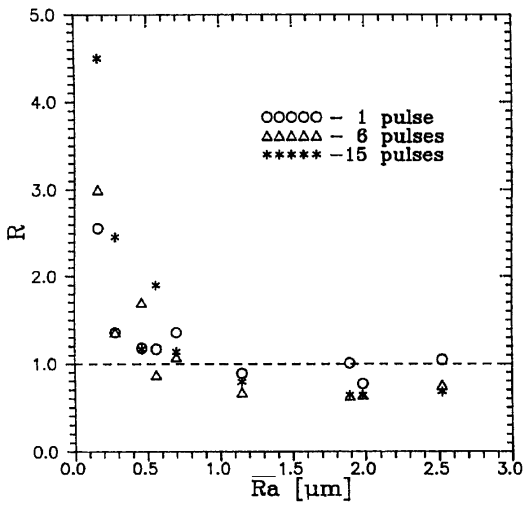

Fig. 6. The ratio of the final to the initial roughness *vs.* the initial roughness for nitrogen plasma pulse treatment of the type 45-type constructional steel [12].

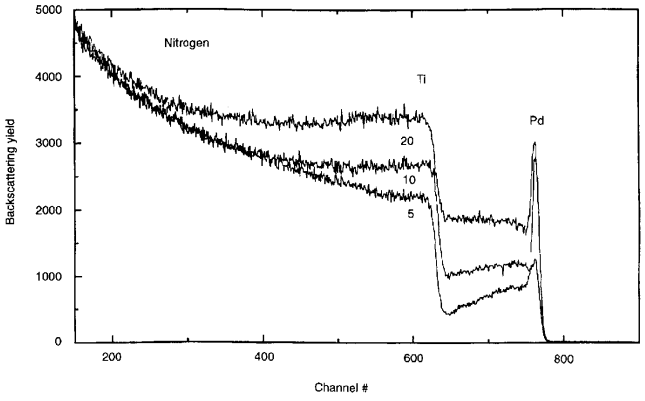

Fig. 7. The RBS spectrum of Ti foil treated with different number (5, 10, and 20) of pulses of nitrogen plasma containing Pd [15].

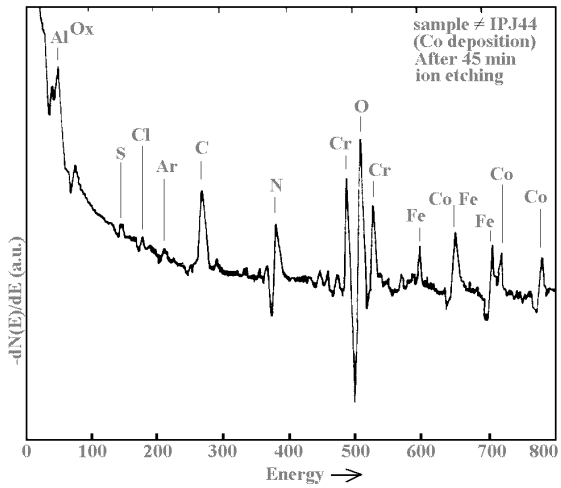

Fig. 8. The Auger spectrum of the sub-surface layer of AISI 321 stainless steel, which was treated with nitrogen plasma streams containing Co from the additional metallic plasma source.

a prolonged ion implantation and usually they result in an increase of a microhardness (by a factor 2.3 of the 45 type constructional steel). Consequently, the wear resistance of steel increases. In the case of constructional steels 40H and 12HN3A, treated with the nitrogen pulses, this increase amounts to factors 3.4 and 1.6, respectively [6].

A low roughness of a treated surface is a very important factor for many practical applications. It is known that a treatment of smooth solid-state surfaces with high-intensity pulsed beams leads to an increase in the surface roughness. On the other hand, an effect of the glazing or smoothing may appear on rough surfaces. This is shown in Fig. 6, where the ratio of the final to the initial roughness is plotted *vs.* the initial roughness. It can be seen that for the small initial values of roughness, the pulse treatment leads to deterioration of the initial roughness, but starting from values around 0.5–1 μm, a prolonged plasma-pulse treatment leads to an improvement [12].

The surface modification by means of metallic or gas-metallic plasma, seems to be a very perspective and flexible method of improving surface properties of metals and ceramics. We have shown that, for the DPE mode the mixing of Al and Ni into a Cu substrate [4], Pd into Ti [15], Cu and Ti into steel, as well as Ti into Al_2O_3 or Ni into Si_3N_4, can be successfully realized. As an example, Fig. 7 shows the RBS spectrum of a Ti foil treated with pulses of nitrogen plasma containing Pd ions. A tail extending on the left of the surface peak of Pd is evidence of the effective mixing of Pd with the substrate.

The deposition and mixing of Ni into Si_3N_4 ceramics lead to significant increase of a wear resistance [10]. The use of the DPE process for the preparation of metallic coatings gives a possibility of improving the adhesion, as a result of a high-temperature mixing in the molten phase. It was also shown that with the use of the separate metallic plasma source, installed in the central part of the working chamber, the effective mixing and thick coating of cobalt, titanium and tungsten on steels, are possible [5]. To demonstrate this effect, Fig. 8 shows an Auger spectrum of the sub-surface layer of AISI 321 stainless steel, treated with pulses of nitrogen plasma containing Co from the metallic plasma source. The spectrum shows that (apart from Co and N lines originating from the plasma-supplied deposit) the lines of Fe and Cr are also observed. The presence of these lines confirms the mixing of Co with the substrate material. On the other hand, such a mixing is possible only if Co ions reach the substrate surface while it is molten.

It is well known that a surface cleaning before the coating is a crucial, tedious and time-consuming step, determining the coating adherence. The pulse plasma treatment is an extremely effective way of the surface cleaning, since it combines an ultimately high-temperature treatment in vacuum and the massive ion bombardment. At the same time, when it is applied in the DPE mode, this enables to prepare intermediate layers for further PVD deposition. Therefore a combination of DPE source for surface cleaning and interface preparation, and PVD equipment for coating in vacuum chamber, makes it possible to obtain highly adherent TiN and other hard coatings on high speed steels, as well as on ceramics [2].

Conclusions

The review presented in this paper enumerates various versions of the surface modification with pulsed plasma streams, developed in SINS. The most important applications are as follows:

- the formation of large area p-n junctions and ohmic contacts in silicon,
- the doping of steels with nitrogen, combined with the simultaneous surface recrystallization,
- the preparation of mixed surface layers on metals and ceramics, up to the formation of surface alloys,
- a pretreatment of metals and ceramics for the PVD coatings (cleaning and intermediate layers).

In view of the method flexibility, as regards the choice of elements involved in the treatment and the potential for a large area processing, the experience accumulated till now is likely to find practical applications in the near future.

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