Electrode erosion mechanism in the rod plasma injector type of generator as deduced from the structure of irradiated substrates

Jerzy Piekoszewski,
Jacek Stanisławski,
Rainer Grötzschel,
Wolfgang Matz,
Jacek Jagielski,
Władysław Szymczyk

Abstract Titanium atoms were alloyed into a polycrystalline alundum substrate using a various number of intense pulses consisting of plasma of the working gas and vapor and low energy ions of Ti eroded from electrodes of the rod plasma injector type generator. It appears that at a single pulse titanium always forms a thin metallic film not mixed with the substrate material. With increasing number of pulses the amount of titanium atoms mixed into the substrate increases, whereas the thickness of the film – decreases. Analyses of phase composition and of structural properties, as well as computer simulations of thermal evolution brought the present authors to the conclusion that increase of number of pulses leads to decrease of melting temperature of the top layer of the substrate. It has also been confirmed that metallic ions eroded from electrodes do not undergo such acceleration like working gas ions do; their energy remains on the 200–300 eV level. It is concluded that erosion of the electrode material occurs during the last phase of the discharge via the vacuum arc mechanism.

J. Piekoszewski✉
Department of Materials Modification and
Department of Plasma Physics and Technology,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock-Świerk, Poland, and
Department of Nuclear Methods of Material Engineering,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22/ 718 06 03, Fax: +48 22/ 779 34 81,
e-mail: jpiekosz@ipj.gov.pl

R. Grötzschel, W. Matz
Institut für Ionenstrahlphysik und Materialforschung,
Forschungszentrum Rossendorf,
Postfach 51 01 19, D-01314, Dresden, Germany

J. Stanisławski, J. Jagielski, W. Szymczyk
Department of Materials Modification and
Department of Plasma Physics and Technology,
The Andrzej Sołtan Institute for Nuclear Studies,
05-400 Otwock-Świerk, Poland

Introduction

Pulsed laser, electron, and ion or plasma beams are known as tools that can be used to promote liquid phase reactions in the near-surface layer of practically any kind of condensed matter. The pulse duration is usually in the nano- to micro-second range and their power density within in the 10^6–10^9 W/cm^2 range. Treatment of solids with high intensity pulsed ion beam (HIPIB) or high intensity pulsed plasma beam (HIPPB) has some features in common with ion implantation, since a mass transport takes place, and some features of laser processing, since heat transport and hence melting of the near-surface layer occurs. In the literature published thus far the HIPIBs are usually generated by magnetically insulated high voltage diodes [6, 10, 11, 12], whereas HIPPBs are generated in the rod plasma injector (RPI) type of devices [1, 4, 5, 8, 9].

RPI generator used in our laboratory can be run in two modes. In one, referred to as pulse implantation doping (PID), the plasma pulses contain almost exclusively ions of the working gas. In the other mode, referred to as deposition by pulsed erosion (DPE), rapid erosion of the metallic electrodes occurs apart from generation of plasma of the working gas. Metal eroded from deliberately chosen electrode forms a well adhering coating that in some cases is mixed into the substrate bulk. In this context, it has been interesting to understand the mechanism and kinetics of erosion of electrodes and to get insight into the physical state of the eroded matter.

Main conclusions drawn from our previous experiments [9] with various working gases (N, Ar, Xe) and metallic electrodes (Ti, W) were twofold: first, metal atoms eroded

from electrodes do not undergo ionization and acceleration during the discharge in the same way as it is the case with working gas. Second, erosion of electrodes is caused by some thermal effects rather than by sputtering. First conclusion was inferred from the fact that RBS spectra of Al_2O_3 samples irradiated by a single pulse in the DPE mode exhibit a sharp symmetric surface peak of Ti (from titanium electrodes) for both N working gas (with lower atomic mass than Ti), and Xe working gas (with higher atomic mass than Ti). In both cases no mixing of Ti with the substrate occurred. On the contrary, mixing was evidently visible for both working gases when two pulses were applied. This means that independently of the atomic mass of the working gas the first pulse deposits Ti atoms on a solidified substrate; the Ti film remains unmixed until the subsequent pulse. Titanium atoms might arrive too late in respect to nitrogen ones in order to mix with the nitrogen--melted substrate surface even if titanium atoms were ionized and accelerated like the working gas N atoms are. However, such possibility is excluded in case of much heavier xenon: titanium ions would have to arrive before xenon ions and consequently would have to be mixed already after the first pulse. Lack of mixing after the first pulse indicates that titanium must have traveled towards the substrate slower than xenon. The possibility that eroded metallic atoms are ionized and accelerated like working gas atoms is therefore excluded from further considerations.

"On-line" spectrometry of the eroded atoms/ions is very difficult due to plasma and huge electromagnetic field present during discharges. Therefore, in the present work we attempted to get some information on state of the eroded metal by careful analysis of its concentration profiles in substrates processed by the DPE technique with different number of pulses. Structural analysis of the near-surface region of substrates was also carried out.

Ti as the deposit and Al_2O_3 as the substrate were deliberately chosen for two reasons. Firstly, from our previous work [9] it is known that perfect mixing of Ti into Al_2O_3 occurs when substrate is in molten state during the DPE process; this simplifies interpretation of the RBS data. Secondly, Ti-Al_2O_3 is the only system so far found by us, in which the thermophysical properties of the substrate are matched to the energy of Ti ions ablated during the DPE process (conducted in RPI generators of the type used in these experiments) as to render the dependence of the surface structure on a number of pulses readily observable. The subsequent sections of this paper shows that the experimentally observed behavior of the near-surface structure of alumina irradiated with different number of HIPPB pulses enables one to speculate about the energy of ions eroded from metallic electrodes during the plasma discharge.

Experimental

The HIPPB treatment was conducted in the DPE mode using the I-46 RPI-type pulse plasma generator. Briefly, in this technique the portion of working gas (e.g. nitrogen) is injected into the inter-electrode space. The electrode system consists of two sets of coaxial rod-type Ti electrodes. After electronically-controlled delay a high voltage is applied to the electrodes, which ignites gas discharge. The

following phases of the discharge can be distinguished:

– Phase I. The gas discharge develops starting from the injecting valve region and during 3 to 4 µs moves axially toward the open end of the electrodes. The axial electromagnetic force is the plasma driving force.
– Phase II. An abrupt breakdown of the discharge current occurs at the end of phase I when ionized gas leaves the inter-electrode space. It induces an overvoltage between the electrodes, reaching 60 kV at the maximum. This phase lasts about 0.15 µs.
– Phase III. When the overvoltage ceases, the gas discharge transforms into the arc discharge between the terminal part of the electrodes (on the length of about 3 cm). The discharge lasts until the end of the second half-period of the current transient i.e. about 10 µs.

As a result of such sequence of the discharge phenomena a pulse of working gas plasma is generated. The discharge results also in ablation of some amount of the electrode material. According to our analysis of electrical transients occurring in the I-46 generator with condenser bank charged up to 29 kV/16.8 kJ, dissipated power density at the eroding end of the electrodes reaches 10^8 W/cm² (average voltage 30 kV, average discharge current 200 kA, dissipation on the electrodes of about 60 cm² area). The pulse lasts about 1 µs and deposits on the target surface (30 cm apart from the electrodes) energy density in the range 1–6 J/cm².

The DPE process proceeds as follows. At first, the nitrogen plasma pulse melts surface of the substrate; it remains melted up to several µs to a depth of 0.1–2.0 µm. Metallic vapor or low energy ions reach the substrate later than the plasma ions. The question whether they condense on the already re-solidified substrate or else diffuse into the molten pool (which depends on relation between travel time of the metallic atoms to the substrate and duration of the molten phase) is still open; it is to be answered – at least partially – by this work.

Over 20 substrates of polycrystalline commercial alumina (99.6% purity) were irradiated with 2, 5 and 10 pulses in the present experiments. In addition, a few samples were treated with 20 pulses. Number of pulses in each set of samples were chosen randomly in order to avoid any effects originating from aging of electrodes.

Samples were characterized by the X-ray diffraction measurements in grazing angle geometry (GXRD) at ω=1° using CuK_α radiation, and by Rutheford backscattering (RBS) technique with ⁴He ion beams of energy 1.7 MeV.

Results and discussion

Figure 1 shows GXRD pattern taken on a sample processed with 20 pulses in the DPE mode; pattern of some untreated alumina substrate is also shown as a reference. Without any doubt the most intense reflections in the modified sample belong to the Al_2O_3 phase. Detailed analysis of the GXRD patterns revealed also evidence for the presence of Al_5O_6N and AlN phases. Phases such as Ti_3AlN and Al_2TiO_5 were identified with a lesser probability. These results are little surprising since the not-observed TiO_x
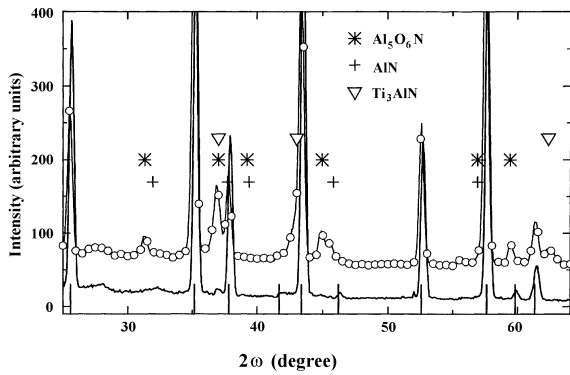
Fig. 1. XRD patterns of alumina substrates. Solid line – untreated; open circles – 20 plasma pulses treated samples.

phase could have also been expected due to strong reactivity of titanium toward oxygen.

Figure 2 shows three RBS spectra for Al_2O_3 samples processed with 2, 5 and 10 plasma pulses in the DPE mode. Each spectrum in this Figure represents an average taken from spectra of 4 samples irradiated with the given number of pulses. For two pulses there is a well pronounced peak (around channel No. 660), which represents Ti atoms deposited on the surface, but not mixed into the bulk. On the other hand, the surface peak practically does not exist for 10 pulses. The tail to the left of the surface peak represents Ti atoms mixed with the substrate.

In order to get insight into evolution of the titanium in-depth profile with the number of pulses, the RUMP program was used to fit the simulated spectra to the experimental data shown in Fig. 2. The results of the fit are shown in Fig. 3, in which the bulk concentration of Ti in at.% (the mean value taken from the distribution beneath the surface down to about 500 nm) and thickness of the Ti film deposited on the surface are shown as a function of the number of pulses. Numerical analysis of the RBS spectra shows that subsequent pulses contribute similarly to the bulk concentration of titanium; mean values are 4.2×10^{15}, 6.7×10^{15}, and

4.8×10^{15} at./cm^2 per pulse for 2, 5 and 10 pulses, respectively. Scatter of the above values can be accounted for by such phenomena as Ti vapor screen effect, some erosion of target material etc. as well as by restricted reproducibility of plasma pulses generated by our generator.

Increase of Ti concentration in the bulk with number of pulses is quite comprehensible in view of the fact that each pulse brings a new dose of Ti atoms that are subsequently mixed into the bulk by the diffusion in liquid state process. However, decrease of the amount of titanium deposited on the surface is less obvious. If the effects of the electrode aging do not play any important role (see the previous section), then this behavior can be accounted for by an increase of molten phase duration with increasing number of pulses. This could be accounted for either by decrease of the melt temperature of the top layer, or by increase of the substrate heat conductivity. We rule out the last possibility from further consideration since bulk of the substrate through which heat sinks does not undergo any modification during the HIPPB processing. Thus we are left with the possibility of change of the top layer melt temperature T_m.

In order to gain some semi-quantitative information regarding relation between T_m and melt duration τ_m, we solved numerically one-dimensional heat flow equation with material parameters for Al_2O_3 taken from the literature. It was assumed that the plasma pulse energy of 4 J/cm^2 was absorbed in an infinitesimally thin near-surface layer of the substrate and the power vs. time transient was of the Gaussian shape with full width at half maximum (FWHM) value equal to 1 μs. In several computation runs all input parameters describing the modified top layer were kept constant except for its melting point: we introduced such "artificial" melting temperature T_m' that the T_m'/T_m ratio was between 0.5 and 1 (melting point T_m for pure Al_2O_3 was taken as 2303 K). The computed τ_m vs. T_m'/T_m depend-
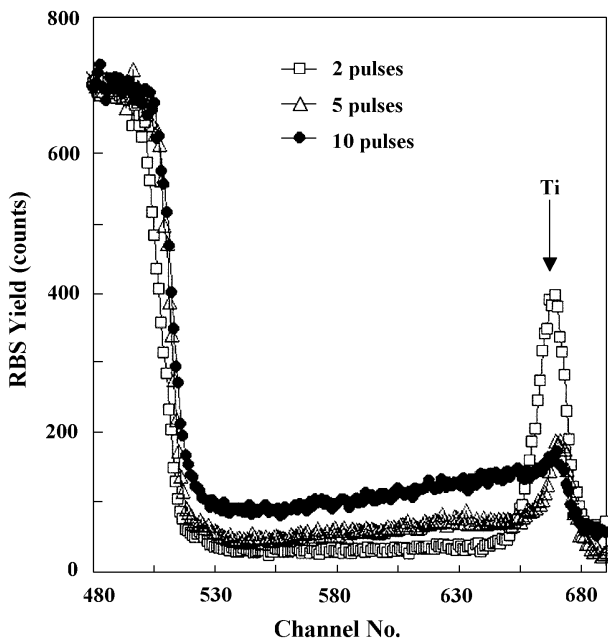

Fig. 2. RBS spectra of Ti/Al_2O_3 structures after treatment with 2, 5 and 10 plasma pulses. Each spectrum represents an average over 5 samples.
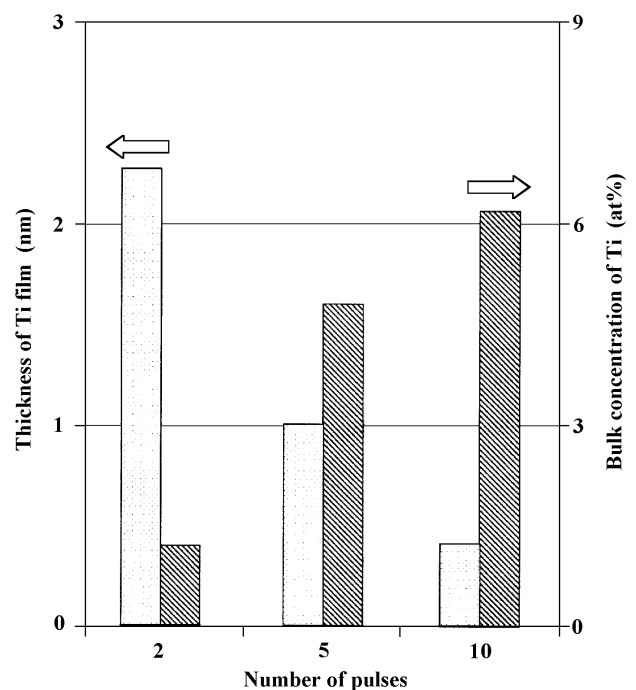

Fig. 3. Ti surface film thickness and Ti bulk concentration (mean value taken from the distribution beneath the surface down to about 500 nm) in Al_2O_3 vs. number of plasma pulses as derived from RBS data.
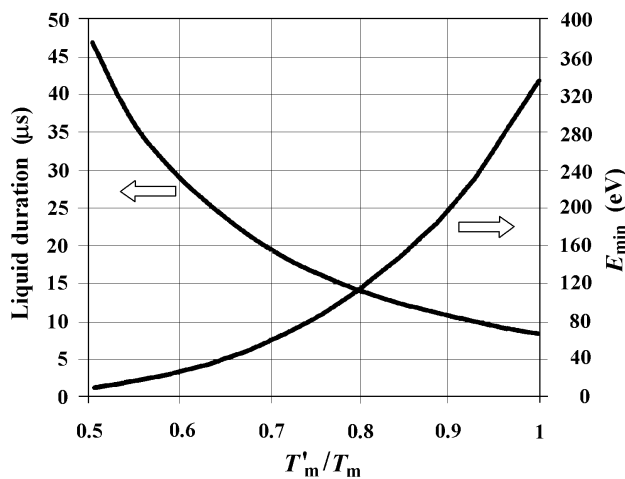
Fig. 4. Calculated melt duration of the top layer of plasma pulse modified Al_2O_3 and minimum kinetic energy necessary for Ti ions to reach melted substrate surface vs. reduced melting temperature.

ency is shown in Fig. 4 together with the values of minimum kinetic energy E_{min} necessary for titanium ions to reach the substrate when its top layer is still melted. In other words ions having kinetic energy greater than E_{min} will travel the distance between the electrodes and the substrate (i.e. 30 cm) in time $t \leq \tau_m$.

As seen from Fig. 4, melt duration $\tau_m = 8$ μs for untreated Al_2O_3 (i.e. for $T_m'/T_m = 1$) corresponds to $E_{min} = 320$ eV. Since the whole amount of Ti remains after the first pulse exclusively on the Al_2O_3 surface (as observed in [9] for N, Ar, and Xe working gases), it seems obvious that kinetic energy of titanium ions/atoms must be lower than 320 eV. To estimate at least the range of average energy of titanium ions/atoms, let us assume that after processing with 10 pulses melt temperature of the top layer of the substrate has been reduced by about 10%, which corresponds to the lowest melt temperature among the phases identified in the XRD measurement. For $T_m'/T_m = 0.9$ the melt duration amounts to 11 μs, which corresponds to $E_{min} \approx 200$ eV. This means that if the average kinetic energy of the expanding Ti ions/atoms were somewhere between 200 and 300 eV, then these ions/atoms would reach the substrate when its top layer is still melted. In such case practically all Ti ions/atoms would diffuse into the bulk leaving no film on the surface, and we would not see any surface peaks in Fig. 2.

In view of these facts it seems interesting to take a look at values of energies of ions/atoms ablated from solids by different energy-carrying beams reported in the literature. For example in [13], the plasma generated by ablation of aluminum and carbon targets irradiated with laser, vacuum arc current, and electron beams of a power density exceeding 10^8 W/cm^2 was analyzed. It was found that in all cases – irrespective of differences in mechanisms of beam-target coupling – conversion from thermal energy of electron gas into kinetic energy of expanding ions takes place and the ion energy is in the 30–250 eV range. In [3], the plasma plums of silicon, germanium, and cooper ablated by irradiation with excimer-laser (KrF 248 nm/25 ns, and ArF 193 nm/17 ns) were examined by the time-of-flight method. Here again, the most probable kinetic energy of ions was found to be between 50 and 100 eV. The authors of [3] state that electrostatic ion-acceleration model can account for their results. Similar values are reported in [7] for iron target

irradiated with 4.5 J/cm^2, 26 ns, 248 nm excimer laser pulses. These data indicate that ionization and some acceleration of ablated vapor always occur for sufficiently high power density dissipated in target material, regardless on the kind of energy carrier and beam-target coupling mechanism.

Therefore, the 200–300 eV range of titanium ion energy estimated in the present work is not surprising. However, the question arises why the metallic ions are not accelerated to much higher (several keV) energies during the discharge as it is the case for the working gas ions. At present, we do not have a fully documented explanation of these observations; the tentative one can be as follows. Atoms of the working gas are ionized as a result of the discharge and are accelerated to high energies during the phase II when the overvoltage develops. In principle, erosion of the electrodes via vaporization and/or ablation processes can proceed in both phases II and III. However, we exclude phase II from further consideration since we have never observed any electrode erosion during the PID process in which the phase II occurs in the same way as in the DPE regime, and phase III does not occur at all. Therefore, it seems obvious that erosion, ionization and acceleration of the electrode material occurs exclusively in phase III of the discharge. If so, one cannot expect acceleration of ions by the overvoltage, since it has already ceased in that phase. On the other hand, ion energies in the range of few hundred eV – as estimated in the present work – fall well into the range of energies determined for plasma in vacuum arcs [13]. Therefore, we finally conclude that electrode erosion in RPI plasma generator occurs via vacuum arc mechanism. If so, the amount of ionized metallic atoms may reach as much as of 90% according to [2].

Conclusions

a) Metallic atoms eroded from electrodes during gas discharge in the rod plasma injector type of generator are not ionized and accelerated in the same way as atoms of the working gas.
b) Energy of metallic ions is likely to be in the range of few tens to few hundreds eV.
c) Most likely the electrode erosion occurs via vacuum arc mechanism.

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