

# Surface treatment of metals in the plasma of a nanosecond diffuse discharge at atmospheric pressure<sup>\*</sup>

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**Abstract.** The paper presents experimental results on surface treatment of metals in the plasma of a runaway electron preionized diffuse discharge (REP DD) in atmospheric pressure nitrogen. The parameters under study are the elemental composition, the nanohardness, the surface free energy (SFE) and the surface roughness of metals before and after plasma treatment. The study shows that REP DD plasma treatment with  $10^5$  discharge pulses provides ultrafine surface cleaning of the treated metals from carbon and increases their surface free energy up to 3 times, whereas the surface nanohardness and roughness of the treated metals remain almost unchanged.

## 1 Introduction

In microelectronics and LED technologies, it is of significance to provide surface cleaning of bond pads and dies from various technological contaminants before wire bonding and packaging assembly. The most efficient and widely used method of such surface cleaning is treatment in the plasma of a radio frequency (RF) or a microwave (MW) discharge [1]; these types of discharge are, as a rule, formed in Ar, O<sub>2</sub> or their mixtures at low pressures measuring 0.2–2 Torr. In one of the recent studies, LED gold bond pads were exposed to plasma treatment in RF and MW discharges in argon at a gas flow rate of 30 mL/min to compare two types of treatment in terms of their efficiency of contaminant removal and quality of bond interface adhesion [2]. The results demonstrate that plasma treatment in a MW discharge provides more efficient removal of surface contaminants and better surface quality than plasma treatment in an RF discharge.

Due to the high price of gold, semiconductor companies consider the use of alternative wire bonding materials, and some of them have already adopted gold-free wire bonding technologies [3,4]. Here we present experimental results on surface treatment of metals in the plasma of a runaway electron preionized diffuse discharge (REP DD) in atmospheric pressure nitrogen in repetitive pulsed mode [5]. This type of discharge can be generated in different gases at atmospheric pressure by applying nanosecond high-voltage pulses to the gap between a sharp-ended cathode

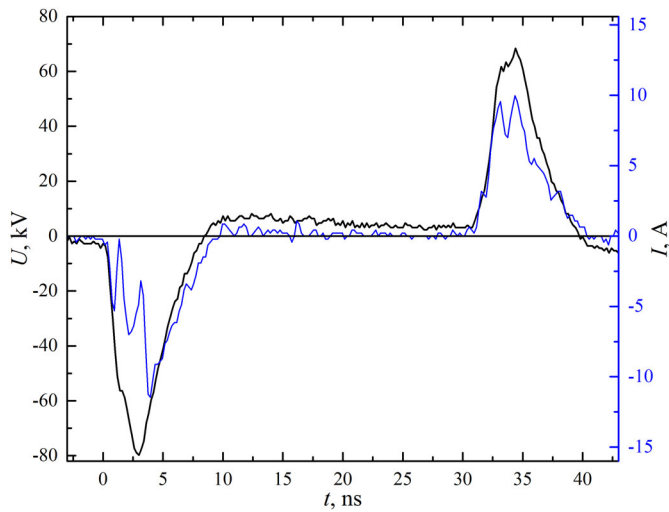
and a plane anode. According to measurement data, the maximum electron concentration in the plasma of a repetitive pulsed REP DD in atmospheric pressure nitrogen is attained in the middle of the gap and is  $\sim 4 \times 10^{14} \text{ cm}^{-3}$  at a gas temperature of 820 K [6], being comparable with the characteristics of RF and MW plasmas. The devices used to produce REP DDs are simple in design, requiring neither vacuum chambers nor gas pumping systems, and this makes the REP DD very promising for application in technologies of surface treatment of materials, including heat sensitive materials, for microelectronics and medicine.

Research data on REP DD treatment of stainless steel and copper in pulsed (1 Hz) and repetitive pulsed (2 kHz) modes using RADAN-220 and NPG-15/2000N generators (200 kV and 30 kV, respectively) demonstrate surface cleaning of the materials from carbon contaminants and their surface oxidation to a depth of  $\sim 30$  nm both in air and in nitrogen [7]. However, the pulse repetition frequency of RADAN generators is low, and hence, a longer treatment time is required to attain the desired results compared to lower-voltage repetitive pulsed generators. According to another study [8], REP DD treatment of copper in air can cause, in addition to carbon removal and oxidation, an increase in its surface free energy from 21 mJ/m<sup>2</sup> to 62.5 mJ/m<sup>2</sup>.

Here we continue the research [7,8] and investigate the effect of surface treatment of copper (Cu), stainless steel, aluminum (Al), niobium (Nb), and titanium (Ti) in the plasma of a REP DD in nitrogen by measuring the elemental composition of the materials (Auger spectrometry), their nanohardness (nanoindentation), surface roughness (profilometry), and surface free energy (water contact angle measurements according to the Owens-Wendt method)

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**Fig. 1.** Waveforms of the voltage (black) and discharge current (blue).

before and after REP DD treatment. The use of repetitive pulsed diffuse discharges provides much shorter treatment times compared to other methods [7,8], and the use of nitrogen, unlike air [7,8], precludes the formation of oxide layers on metals [7,8].

## 2 Experiment

In our experiments, we used a GIN-100-1 voltage generator (Antares Ltd., Russia) and a discharge chamber the design of which is described elsewhere [9]. For the formation of a REP DD, negative voltage pulses with a FWHM of 4 ns, amplitude of up to 80 kV, and pulse repetition frequency of up to 100 Hz were applied to an electrode with a small curvature radius (sharp-ended electrode). Figure 1 shows typical waveforms of the voltage and discharge current. The first voltage pulse is the sum of an incident wave and a wave reflected from the discharge gap. The second voltage pulse is the first pulse reflected from the discharge gap to the generator, then reflected from the generator with reversed polarity and returned to the discharge gap. Thus, we have a sequence of voltage pulses of both polarities in the discharge gap, ensuring the effect of electrons and positive ions on the plane electrode.

The plane anode (treated specimen) was shaped as a cylinder of diameter 14 mm and height 2 mm. The anode material was Cu (M1), Al (AD), stainless steel (ST3PS8), Ti (VT1), and Nb (NB1). The interelectrode gap was 8 mm; the mean input power was up to 2 W.

The experiments were performed so that the effect of oxygen on the specimen surface would be minimal. Therefore, the specimens before plasma treatment were mechanically polished with an emery paper, finally polished with diamond suspensions to a mirror surface, and then immediately placed in an ultrasonic bath (Elmasonic S 10H, Elma Schmidbauer GmbH, Germany), rinsed twice with alcohol at 50 °C, and transferred to the chamber for REP DD plasma treatment in commercial nitrogen

(N<sub>2</sub> – 99.5%, O<sub>2</sub> – 0.5, H<sub>2</sub>O – 0.02 mg/L) at a gas flow rate of 5 sL/min. After plasma treatment, the specimens were placed in a sealed container filled with argon and were passed for Auger spectrometry. The concentrations of main chemical elements in surface layers of the materials before and after plasma treatment were measured with a Shkhuna-2 Auger spectrometer and a DFS-458C atomic emission spectrometer (Tomsk Polytechnic University, Russia).

The surface free energy (SFE) before and immediately after plasma treatment was estimated by contact angle measurements with an optical microscope (LOMO MIKMED-1 Version 2, Russia) and was calculated as the sum of polar and dispersive components by the Owen-Wendt method [10] through solving the system of OWRK equations for two different liquids with known dispersive and polar components:

$$(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2} = 0.5 \gamma_L (1 + \cos \theta), \quad (1)$$

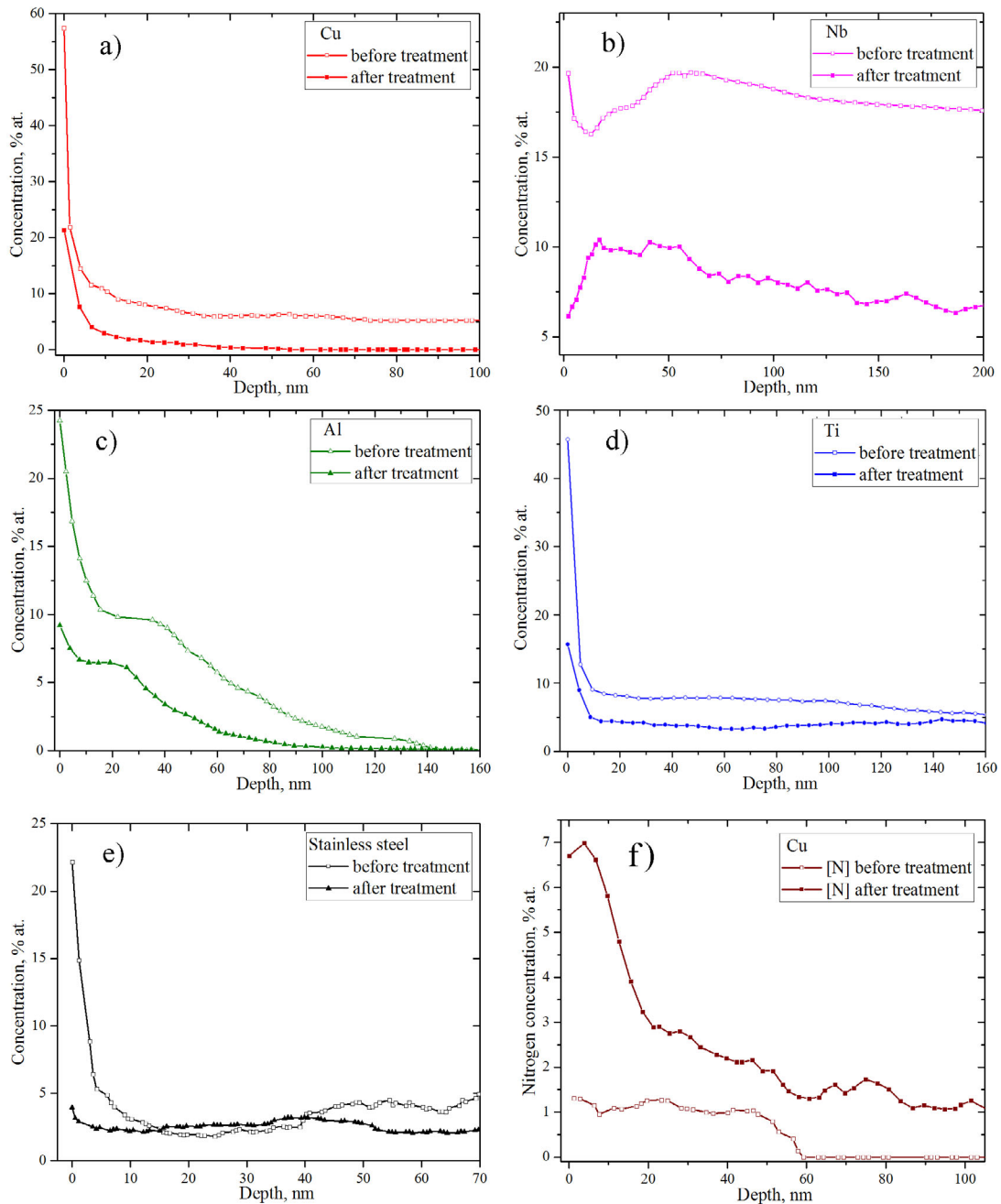
where  $\theta$  is the contact angle of a liquid,  $\gamma_L$  is its total SFE,  $\gamma_s^p$  and  $\gamma_s^d$  are the polar and dispersive components of the metal SFE, and  $\gamma_L^p$  and  $\gamma_L^d$  are the polar and dispersive components of the liquid SFE. For contact angle measurements, deionized water and then glycerine, each in amount of 3  $\mu$ L, was dropped onto the metal surface at room temperature.

The nanohardness of the specimens before and after plasma treatment was measured using a NanoTest 600 system with a Berkovich indenter at a load of 2, 5, 10, and 20 mN with an analysis of loading-unloading curves by the Oliver-Pharr method [11]. The surface roughness was measured using a Micro Measure 3D Station (STIL, France).

The voltage across the discharge gap was measured with a capacitive divider, and the current was measured with a resistive shunt with data transmission to a Tektronix MDO3104 oscilloscope (bandwidth 1 GHz, time resolution 5 GS/s).

## 3 Results and discussion

Figure 2 shows concentration profiles of carbon in surface layers of Cu, Nb, Al, Ti and stainless steel before and after plasma treatment with 10<sup>5</sup> pulses. It is seen from the figure that the best cleaning effect after plasma treatment was attained for the Cu specimen. The carbon concentration in near-surface layers of Cu decreased from 60 at% to 20 at%, and at a depth larger than 10 nm, it decreased 5 times. The carbon concentration in the Nb specimen after treatment was  $\sim$ 2.5 times lower than that before treatment. The carbon concentration throughout the depth of the Al specimen after plasma treatment was about half the concentration before treatment. In the Ti specimen, the carbon concentration decreased 3 times (from 45 at% to 15 at%) in its upper layer and 2 times (from 8 at% to 4 at%) at a depth larger than 19 nm. In the untreated stainless steel specimen, carbon was found only in near-surface layers and its concentration was about 22 at%,



**Fig. 2.** In-depth concentration of carbon for Cu (a), Nb (b), Al (c), Ti (d), and stainless steel (e) before and after plasma treatment with  $10^5$  pulses; and nitrogen concentration for Cu before and after plasma treatment with  $1.6 \times 10^5$  pulses (f).

and after plasma treatment the carbon concentration was below 5 at%, which is close to the sensitivity limit of the Auger spectrometer.

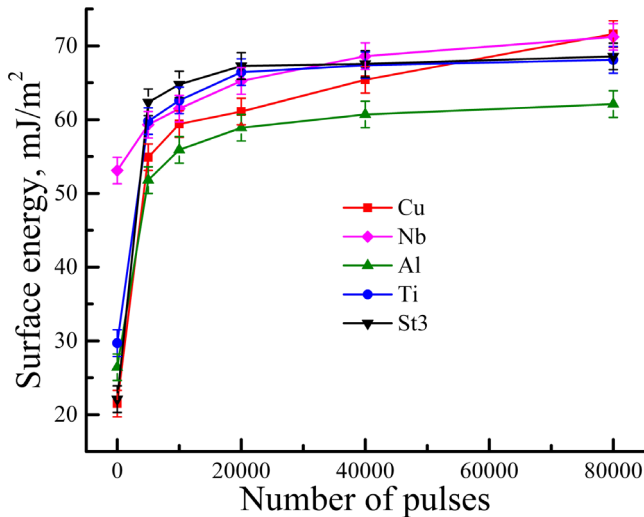
The nitrogen concentration in a Cu near-surface layer 10 nm thick after plasma treatment increased slightly (up to  $\sim 5.5$  at%) and grew slowly with increasing the number of pulses. To verify it was the plasma, rather than the measurement error of the Auger spectrometer, that built up the nitrogen concentration in Cu, we increased the number of pulses to  $1.6 \times 10^5$  (Fig. 2f); in the other metals, the increase in nitrogen concentration was negligible.

The mechanisms of surface cleaning from carbon contaminants can be the following: through a physical reaction between carbon and nitrogen molecules and ions excited in collisions with electrons in the gas discharge and through chemical reactions such as decomposition of carbonates by thermolysis and hydroxides by oxidation due to oxygen present in the commercial nitrogen and at the chamber walls:



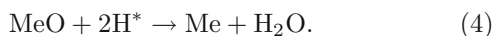
**Table 1.** Dispersive, polar, and total surface free energies for five metals treated with 80 000 pulses.

	Before treatment			After treatment		
	$\gamma^d$ , mJ/m <sup>2</sup>	$\gamma^p$ , mJ/m <sup>2</sup>	$\gamma$ , mJ/m <sup>2</sup>	$\gamma^d$ , mJ/m <sup>2</sup>	$\gamma^p$ , mJ/m <sup>2</sup>	$\gamma$ , mJ/m <sup>2</sup>
Cu	11.7	9.8	21.5	30.6	40.9	71.5
Nb	10	15.2	25.2	32.5	38.7	71.2
Al	15.9	10.5	26.4	28.2	33.8	62.1
Ti	14.9	14.8	29.7	27.2	40.9	68.1
ST3	16	16.3	32.3	29.9	38.7	68.6

**Fig. 3.** Surface free energy versus the number of pulses for Cu, Nb, Al, Ti, and stainless steel.

where Me corresponds to a metal atom.

The water produced in reaction (3) dissociates into OH<sup>-</sup> and H<sup>+</sup>, and the hydrogen ions provide a reduction reaction of the metal, thus contributing to surface cleaning:



However, the above physical and chemical mechanisms cannot fully explain the decrease in carbon concentration in the metal bulk (at a depth larger than 20–30 nm), and the causes for the decrease require further investigations. Possibly, the decrease can be associated with specific features of the Auger spectrometer.

Thus, the surface concentration of carbon and hydrocarbons with a weak polar C-C/H bond decreases, and this increases the surface free energy, thereby decreasing the contact angle.

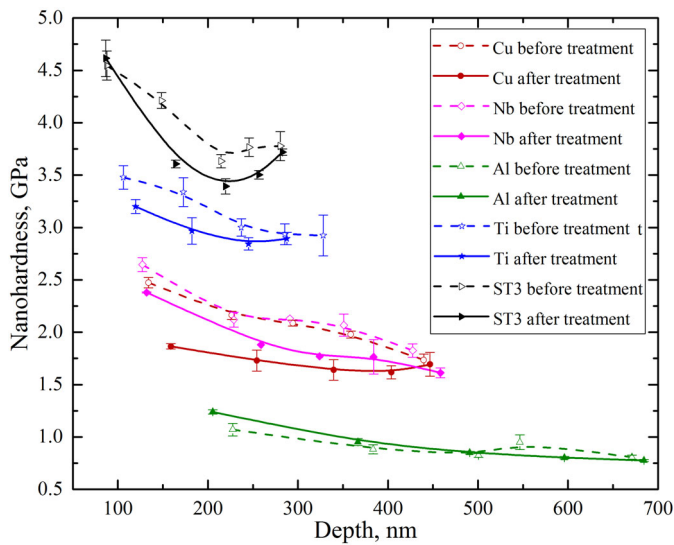
It can be seen in Figure 3 that early in the plasma treatment, the SFE increases steeply, and as the power and the number of pulses are increased, its increase slows down. Before plasma treatment, the SFE of the Cu specimen is 21.5 mJ/m<sup>2</sup> and increases to 55 mJ/m<sup>2</sup> (by 255%) and 71.5 mJ/m<sup>2</sup> (by 330%) after plasma treatment with 5000 and 80 000 pulses, respectively. The total SFE and its dispersive and polar components calculated by equation (1) for the metals before and after plasma treatment with 80 000 REP DD pulses are presented in Table 1.

As can be seen from Table 1, the most significant increase in the SFE after plasma treatment is attained for Cu and Nb: their surface free energy increases 3.3 and 2.8 times, respectively. The increase in the SFE for Al, Ti, and stainless steel is smaller: 2.4, 2.3, and 2.1 times, respectively. These data confirm the results of Auger electron spectroscopy, showing that the higher the quality of surface cleaning, the larger the increase in the SFE. In all cases, except for Nb, the increase in the polar component of SFE is more considerable than the increase in its dispersive component. The polar component of SFE in a solid represents strong interactions and hydrogen bonds typical of organics compounds, and its dispersive component represents Van der Waals forces (dipole-dipole interactions) and other nonspecific intermolecular interactions (e.g., electrostatic) which are insufficient to break or form new chemical bonds. Hydrophobic surfaces feature a high content of -CH<sub>x</sub> groups, and hence, their SFE is low. When such a surface is exposed to high-energy runaway electrons produced in a REP DD with bombardment by nitrogen ions, the -CH<sub>x</sub> groups are decomposed and carbon is removed from the metal surface and near-surface layers, resulting in free hydrogen bonds and surface saturation with hydrogen, which increases the SFE. The surface saturation with hydrogen slows down with depth, thus slowing down the increase in SFE (Fig. 3). Another factor that can increase the SFE is the formation of OH groups with polar covalent bonds on the surface. However, the data of Auger spectroscopy reveals only a slight (no more than 5 at%) increase in the oxygen content on the surface of Al, Ti, and Nb, which are always covered with a thin layer of native oxides (Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>) preventing their in-depth oxidation. In more corrosion-resistant Cu, the oxygen concentration decreases slowly with increasing the number of REP DD pulses, and after 4 × 10<sup>5</sup> pulses, any oxygen on the Cu surface is not found at all. The hydrogen concentration, which is impossible to measure by Auger spectroscopy, was estimated with an atomic emission spectrometer and the data demonstrated an almost twofold increase in the hydrogen concentration after exposure to 10<sup>5</sup> discharge pulses.

The nanohardness of the specimens after plasma treatment remains almost unchanged, as evidenced by nanoindentation (Fig. 4). The surface nanohardness of Cu after treatment decreases by 20%, and the nanohardness of stainless steel, Nb, and Ti decreases by 10%; the changes in the Al nanohardness is negligible.

The decrease in nanohardness, as opposed to [8], is likely due to the absence of oxide formation and to the rise





**Fig. 4.** Nanohardness of the metal specimens before and after plasma treatment with  $10^5$  pulses.

of tensile stress in a thin surface layer with low-angle misorientations of fragments under discharge-induced thermal deformation. This issue requires complex microstructure research by transmission electron microscopy and X-ray analysis, which is a subject of our further studies.

The average surface roughness  $R_a$  after treatment changes by no more than several percent from its initial values. For example,  $R_a$  for Cu decreases from 21 nm to 18 nm.

Thus, REP DD plasma treatment in nitrogen provides an increase in surface free energy and removal of contaminants, thus increasing the bondability and reliability of different interconnections and enhancing the film adhesion. The use of REP DD plasma for surface cleaning has a series of advantages over other treatment methods, e.g., heat treatment in vacuum with hydrogen plasma [12]. First, it is the possibility to realize the process at room temperature, which is significant for some medical applications. Second, no expensive vacuum equipment is required, and plasma treatment in situ is possible.

## 4 Conclusion

Thus, we have investigated the effect of surface cleaning of metals in the plasma of a runaway electron preionized diffuse discharge in atmospheric pressure nitrogen. The surface cleaning is due to bombardment of  $\text{CH}_x$  molecules by nitrogen ions, to high energy runaway electrons and

to plasma chemical reactions with hydrogen. The data of Auger electron spectroscopy and contact angle measurements demonstrate that the higher the quality of surface cleaning, the larger the increase in the surface free energy. The nanohardness and the roughness of the treated metals remain almost unchanged. The decrease in the nanohardness is likely due to tensile stresses arising in a thin surface layer during REP DD treatment. The research results show that the plasma of a REP DD provides high-quality surface pretreatment of metals without any mechanical damages, which is important for further bonding, adhesive coating deposition, and printing.

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## Author contribution statement

All authors contributed equally to the paper.

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