Optical Emission Spectroscopy and Contact Angle Study of Plasma Cleaning of Titanium Alloy Surfaces: Argon Plasma

Jordan Katz,[1,*] Sophia Gershman,[2] & Abraham Belkind[1,2]

[1]Orthobond Inc., North Brunswick, NJ 08902; [2]A. Belkind & Associates, LLC, North Plainfield, NJ 07060

*Address all correspondence to: Jordan Katz, Orthobond Inc., 671 US Hwy 1, North Brunswick, NJ 08902; Tel.: 732 729 6235; Fax: 973 476 9085; katzj@orthobond.com

ABSTRACT: Plasma cleaning is common in the preparation of titanium medical devices. In this study, we examine the use of continuous in situ measurements with optical emission spectroscopy (OES) during plasma cleaning and wet contact angle as a tool to assess titanium implant cleanliness. Plasma cleaning was performed in argon plasma at 66.7 Pa in a commercially available radio-frequency (RF) power plasma system using 25 or 100 W of power. During cleaning, the intensities of OES lines at 386 and 418 nm, as related to surface contaminants, decreased over time and reached a baseline level in ~1 h. However, the water contact angle (WCA) decreased more rapidly, reaching ≤10 degrees in 3–5 sec and further decreased to the limit of detection of ~1 ± 1 degree in 20 min using 25 W plasma and in 1 min using 100 W plasma. The OES data indicate that plasma cleaning starts with rapid removal of contaminants from pronounced regions that are better exposed to the plasma and is followed by prolonged cleaning related to the removal of contaminants from less accessible regions. The delayed rise in WCA demonstrates a limitation in using that technique to assess cleanliness and shows how OES is a useful tool to better understand and control plasma cleaning of titanium surfaces.

I. INTRODUCTION

Titanium (Ti) and Ti alloy have excellent biocompatibility and corrosion resistance and are widely used in medicine for various implants.[1–3] Successful implantation of these materials in the human body requires a baseline level of cleaning to allow for a consistent biological response to the substrate. Failure to achieve this baseline has in the past led to serious medical complications, necessitating tight adherence to cleaning protocols. In some cases, exhaustive cleaning is required, such as when covalent functionalization of the surface with self-assembled monolayers (SAMs) is desired.[4] Typically, the wet contact angle is used to quickly assess the cleaning of a titanium part, and X-ray photoelectric spectroscopy (XPS) is often used as a more sensitive measure of cleaning, although this technique is both expensive and slow. In this study, we apply optical emission spectroscopy (OES) as a tool to rapidly and sensitively assess the cleaning of medical grade, commercially pure (CP) Ti parts.

The surface of Ti and its alloys, as well as many other implantable metals stored in an open environment, consists of a complicated multilayer structure that could include
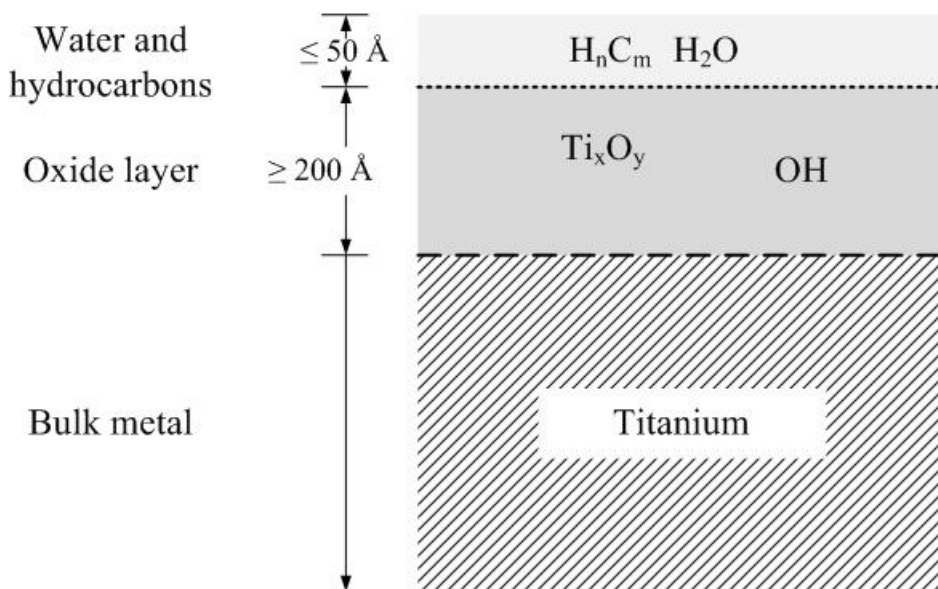
FIG. 1: Idealized surface structure of titanium exposed to clean air.

natural and industrial contaminants. Natural contaminants may include water, hydrocarbons, and various oxides mixed with hydro-oxides (Fig. 1). In addition, a metal surface can contain traces of common air pollutants such as carbon monoxide, sulfur oxides, nitrogen oxides, atmospheric hydrocarbons, and lead. Industrial contaminants can include water, cleaning solutions, organics, lubricant oil, and detergents. Cleaning of Ti and Ti alloys is often done by a combination of wet chemical and dry plasma processes. As a first step, wet cleaning removes most of the industrial contaminants but can leave traces of organics and water.[3,5] The second step, dry cleaning, is done under vacuum using, for example, low-pressure gas plasma capable of eliminating nearly all natural contaminants.

Plasma cleaning is done by two basic phenomena that lead to surface cleaning: sputtering and etching. Sputtering, a process that dislodges atoms from the surface of a material by collision with high-energy particles, is the most universally applied cleaning process.[6,7] Sputtering removes atoms from most commonly used biomedical metals and their oxides by, for example, Ar ions whose energy exceeds ~30 eV, whereas less energetic Ar ions remove only physically and chemically adsorbed particles whose bonding energies are in the range of <0.5 and 0.5–5 eV, respectively. If a cleaning object is floating and conductive, the energy of ions for inductively coupled plasma (ICP) usually does not exceed 10–20 eV.[8,9] One can expect that for ICP in argon at a pressure of ~66.7 Pa, the average Ar ion energy does not exceed 10 eV. Therefore, in the case of an ICP system containing a floating conductive object, the energy of Ar ions is usually too low to initiate sputtering of the basic metal or oxide, and cleaning by sputtering does not

change the surface roughness substantially and provides removal of only physically and chemically adsorbed species.

In plasma cleaning by etching, atoms or radicals from the plasma chemically react with the surface contaminants to create volatile products that are desorbed from the surface and pumped out via vacuum. A common technique for removal of some organic contaminants is cleaning with oxygen plasma. However, this technique is limited to contaminants with which oxygen and oxygen radicals can react, creating volatile products.

To achieve a high level of decontamination, plasma cleaning of titanium-based surfaces is often performed with low-pressure plasmas using an argon atmosphere.[10–12] Implementation of various surface characterization techniques has shown that low-pressure Ar plasma can be used to remove all native and environmental contaminants.[10]

Control of plasma cleaning in a manufacturing environment can be achieved by continuous in situ measurements of OES and contact angle measurement of the final cleaned surfaces. Implementation of OES for metal cleaning has been described for Al substrates,[13] whereas contact angle measurements have been widely implemented for assessing the cleaning of Ti and Ti alloy surfaces.[5,11,12] OES gives information about the emission lines of the plasma gas or gas mixture. In addition, emission spectra will contain the transient lines characteristic of the organic material extricated from the surface. We hypothesize that close surveillance of these transient spectral lines can allow precise monitoring of the cleanliness of Ti or Ti alloy surfaces.

In this work, plasma cleaning of CP Ti substrates was performed systematically in Ar plasma in a commercial RF plasma system. The cleaning process was characterized by in situ OES and postprocessing contact angle measurements to determine whether OES can be applied to CP Ti as an effective tool for real-time monitoring of the decontamination of titanium parts intended for sensitive medical applications.

II. METHODS

Ti surface cleaning with Ar plasma was investigated by varying the plasma power and plasma exposure time. OES spectra were recorded during cleaning, and characterization of the cleaned Ti surface by WCA was performed just after cleaning and at set intervals postplasma.

Plasma cleaning with Ar was performed in the cylindrical quartz chamber of an ICP AutoGlow system (Glow Research, Tempe, AZ) (Fig. 2). The system, designed to generate an ICP of up to 300 W, was pumped down with an oil-free dry scroll vacuum pump (Edwards Vacuum; model XDS-35) to a base pressure no higher than 30 Pa. Ultrahigh-purity argon and oxygen were used to generate plasma at a pressure in the range of ~50 to 200 Pa.

Samples of CP Ti were cut from a 0.005 inch thick ribbon into 2 × 4 inch test coupons (Trinity Brand Industries, Countryside, IL). Initial wet cleaning of samples included sonication in a detergent followed by rinsing and sonication in water and ethanol. Control ribbon samples were stored in ethanol until time of use. Just before use,
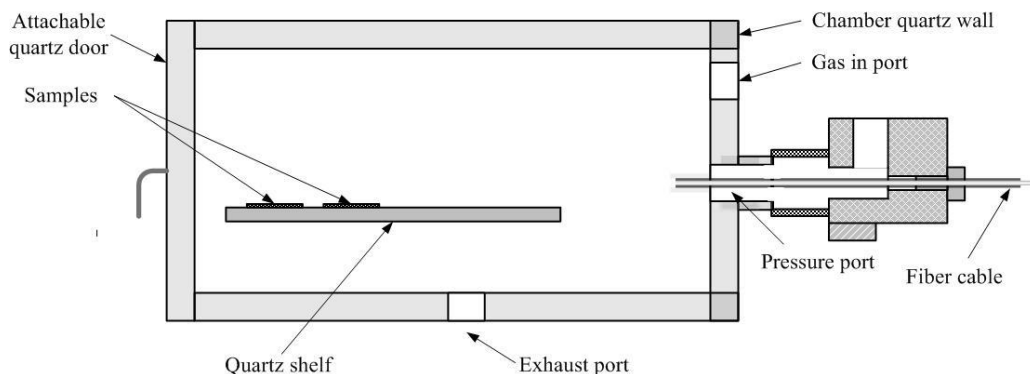
FIG. 2: Schematic of AutoGlow system chamber with installed fiber cable for OES.

control ribbon samples were blown dry under a stream of nitrogen gas and then placed in a vacuum chamber. To prepare phosphonoundecanol (PUL)-treated ribbons, the wet cleaned samples of CP Ti were treated for 5 min in oxygen plasma generated in the AutoGlow system at 25 W and 80 Pa and then dipped into 15 mM PUL (C11H25O4P) in ethanol. These were either used as PUL samples or further treated to produce tethered polymer layer (TPL) Ti + TPL samples.

Plasma cleaning of all samples was performed by placing samples on a quartz shelf located in the middle of the cylindrical chamber (Fig. 2). Before turning on plasma, the system was flushed three times with Ar. The samples were then exposed to argon plasma at an operating pressure of 67 Pa. RF power was set at either 25 or 100 W and samples were cleaned for ≤60 min.

To record optical emission spectra, a specially designed fiber optic cable was inserted into the vacuum gauge port of the plasma chamber and resided about 4 cm from the plasma field (Fig. 2). The fiber optic cable was designed with a 100 μm slit to allow a large amount of light transmission. The cable also had an integrated vacuum ring to prevent vacuum loss after placement into the chamber. Before experimentation, the chamber was routinely cleaned with Ar plasma for 60 min at a pressure of 67 Pa and an RF power of 100 W. Optical emission spectra were measured using a QE Pro scientific-grade spectrometer and OceanView software (Ocean Optics, Bradenton, FL) in the spectral range of 178 to 960 nm. Spectra were recorded every 400 ms, with a collection time of either 40 or 100 ms (as indicated in the Results section, below) per data point.

The surface contact angle between the sample surface and deionized water (WCA) was measured using an Attension model goniometer and Attension Theta software (Biolin Scientific; KSV Instruments). For each measurement, the advancing contact angle was recorded as the average of three successive frames. Three droplets were placed on each sample at each time point, and values were averaged to produce the data as presented. The first measurement of a cleaned sample was performed immediately after its removal from the plasma chamber, with a lag time for placement of samples and execution of measurement of ~1 min. Samples were stored in the open under ambient
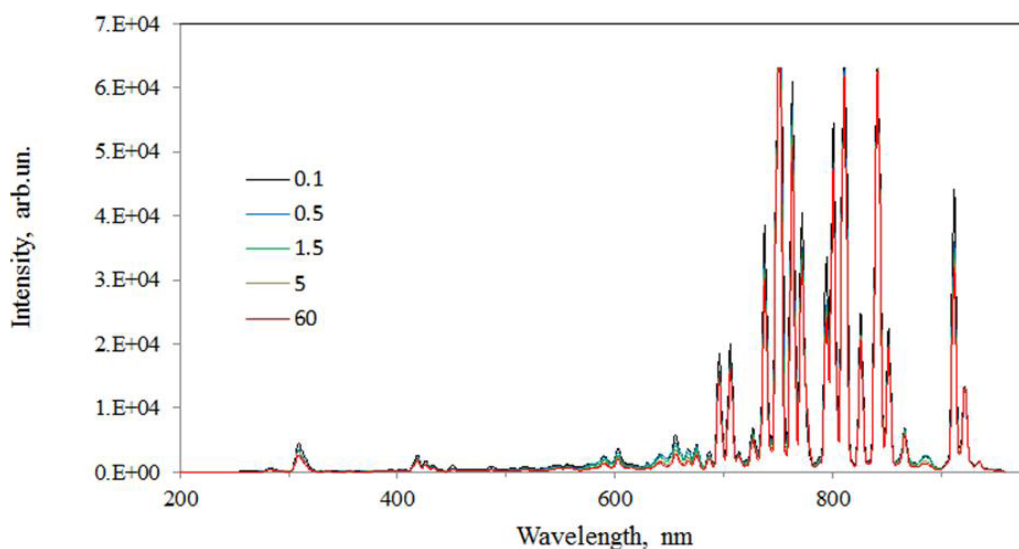
FIG. 3: Optical emission spectra of 100 W Ar plasma while cleaning untreated CP Ti foil. Spectra recorded during cleaning at various indicated plasma exposure times (min).

environmental conditions for the duration of the study, and WCA was assessed at 0 (1 min), 5, 30, 120, and 1440 min on fresh samples at each time point.

III. RESULTS AND DISCUSSION

A. OES of Ar Plasma Cleaning of CP Ti Surfaces.

The complete optical emission spectrum of Ar plasma recorded while cleaning CP Ti coupons is shown in Fig. 3. Spectra were recorded with an integration time of 8 ms, the fastest possible setting of the QE Pro. Nevertheless, some Ar emission peaks were saturated. The obtained optical emission spectrum can be roughly split into two distinct regions: the first includes wavelengths of 600–980 and 260–380 nm, where the spectrum is dominated by peaks related to Ar and N_2; the second region between ~380 and 600 nm includes numerous peaks related to different carbon-containing species. It is in this region, 380–600 nm, where we observed a decrease in the intensity of the peaks as the samples are cleaned and species containing carbon are removed from the samples and then from the chamber. The presence of nitrogen is attributed to residual atmospheric contamination in the chamber and makes determination of plasma parameters very difficult. At a high pressure of 67 Pa, energy transfer from a metastable Ar atom into the excited state of a nitrogen molecule should be considered because it lowers the emission of argon and enhances emission of nitrogen, accentuating the effect of an imperfect vacuum.

To analyze the behavior of peaks within the 380–600 nm region, optical emission
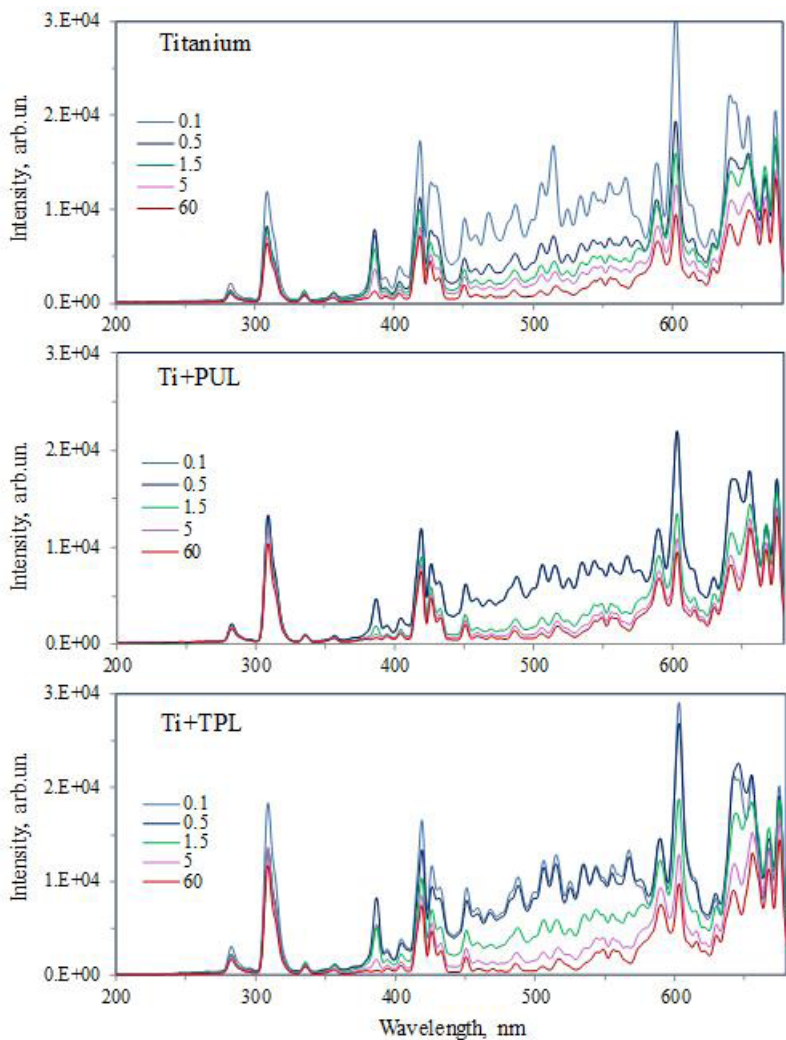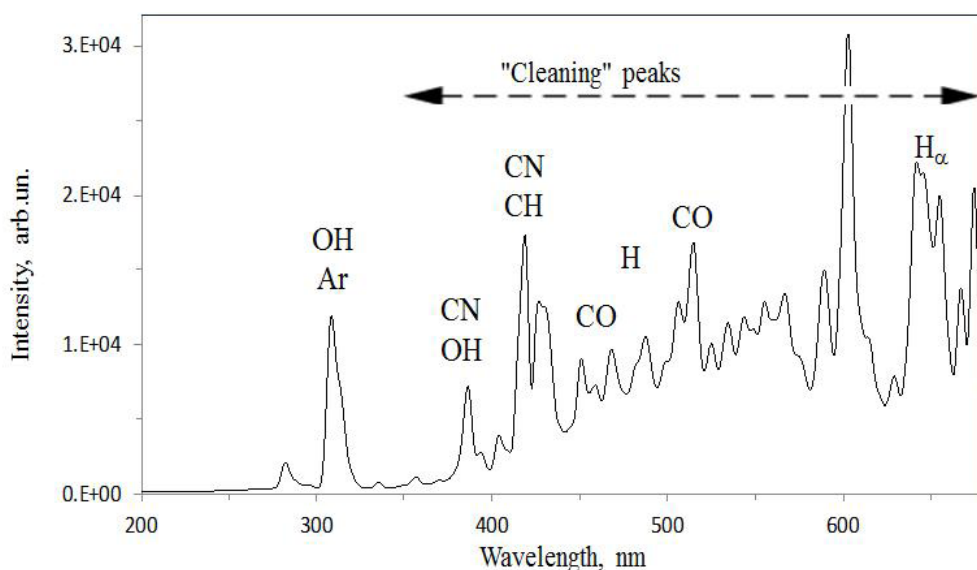
FIG. 4: Optical emission spectra of 100 W Ar plasma while cleaning coupons of un-treated CP Ti foil, coated with Ti + PUL (PAL) and Ti + TPL (TPL). Spectra were recorded during cleaning at various indicated plasma exposure times (min).

spectra of Ar plasma were recorded using a longer integration time of 100 ms while cleaning the untreated CP Ti coupons and the Ti coupons with deposited PUL and TPL layers (Fig. 4). Many of the decreasing peaks in this region belong to different species of carbon and hydrogen atoms and their probable identity, based on previous reports, is shown in Fig. 5. More rigorous studies would be required to establish definitive peak identifications, but it is clear that these peaks are from contaminants that are cleaned from the surface by Ar plasma.

To characterize the cleaning process, decreasing peaks at 386 and 419 nm were

FIG. 5: Optical emission spectra of Ar 100 W plasma while cleaning coupons of un-treated CP Ti foil. Spectra were recorded during cleaning after 5 s of plasma exposure time. Probable emission peak identifications are shown in the graph.

chosen as cleaning reference peaks. Based on the literature, these peaks belong to CN and OH molecules and to CN and CH molecules, respectively.[14] The decrease in peak intensities at 386 and 419 nm as a function of plasma cleaning time and RF power is shown in Figs. 6 and 7. This detailed analysis of the cleaning of CP Ti coupons reveals that, in almost all cases, during the first few seconds the peak intensities increase. This is probably related to both automatic tuning of the plasma system and fast removal of very weakly bonded (physically adsorbed) contaminants. This plasma establishment time increases while going from CP Ti to Ti + PUL and then to Ti + TPL, highlighting the importance of the type of surface contamination for functional cleaning of a Ti surface.

The observed decrease in peak intensities at 386 and 419 nm could be roughly split into two stages composed of an initial fast stage and then a much slower phase, which is consistent with published observations of plasma cleaning of aluminum.[12] The duration of the first stage is inversely proportional to the RF power and lasts for 5–10 min. The dependence of the second cleaning stage on plasma parameters is not clear. But, in all cases, cleaning for about 60 min in Ar plasma, especially when using a power of 100 W, is enough to bring the emission in the "cleaning spectral region" to near-baseline values. We suspect that the first stage of plasma cleaning is related to the removal of contaminants located on the tops of microroughness "mountains," where the electrical field is stronger. Accordingly, the second stage of plasma cleaning is thought to be related to the removal of remaining contaminants, including mainly those located at the bottom of
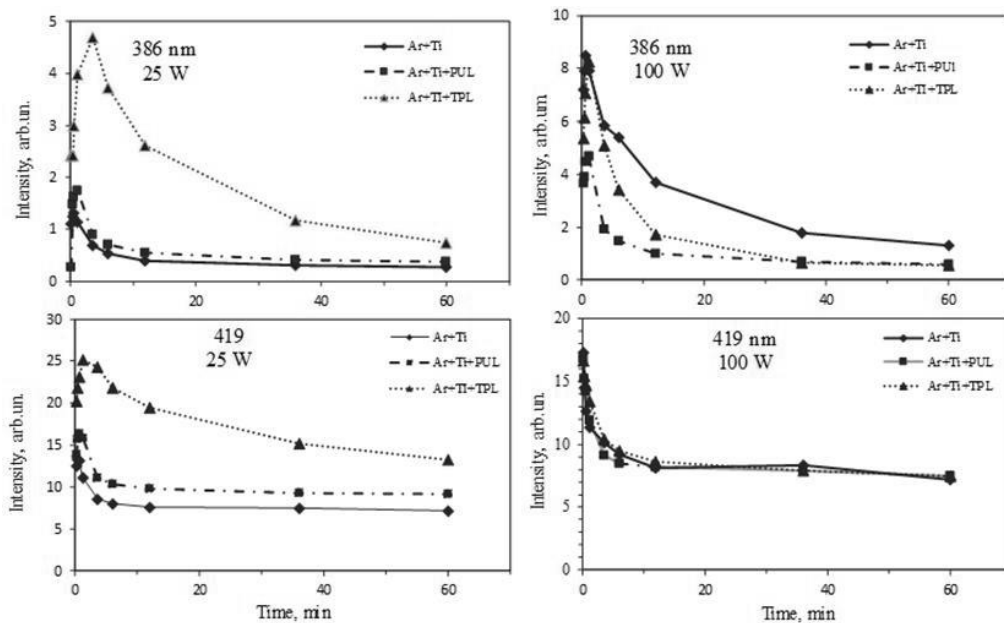
FIG. 6: Optical emission peak intensities of 386 and 418 nm peaks versus plasma cleaning time measured at RF plasma powers of 25 and 100 W.

"trenches," in the regions of microroughness less accessible to plasma cleaning.

Comparing behavior of the 386 and 419 nm peaks shows that the 386 nm signal dissipated more slowly than the 419 nm signal. This difference could be related to OH molecules that are bound more strongly to the surface than C, CN, and CH molecules.

If the excitation of matter etched from a surface-contaminating species of type a is done by inelastic electron collisions, the intensity of a peak intensity I_a seen in a plasma emission spectrum and corresponding to the transition in them ($i \rightarrow j$) could be described as

$$I_a = n_a P_{i,a} \tau_j g_l \tag{1}$$

where n_a is the density of the particles a in the plasma, $P_{i,a}$ is the probability of excitation of the particles in the state i, τ_j is the probability of radiative de-excitation back to the original state i, and g_l is the fraction of emitted photons corresponding to this transition.[13] We can assume that in the first approximation, the concentration of particles n_a in the plasma is proportional to the surface density of these particles on the cleaning surface $N_{a,s}$:

$$n_a = kR_a N_{a,s}, \tag{2}$$

where R_a is the sputtering rate of particles a, and k is a coefficient. Both, R_a and k can depend on the plasma and cleaning surface conditions and can change during cleaning. Therefore, variation of peak intensity I_a with time during cleaning only qualitatively
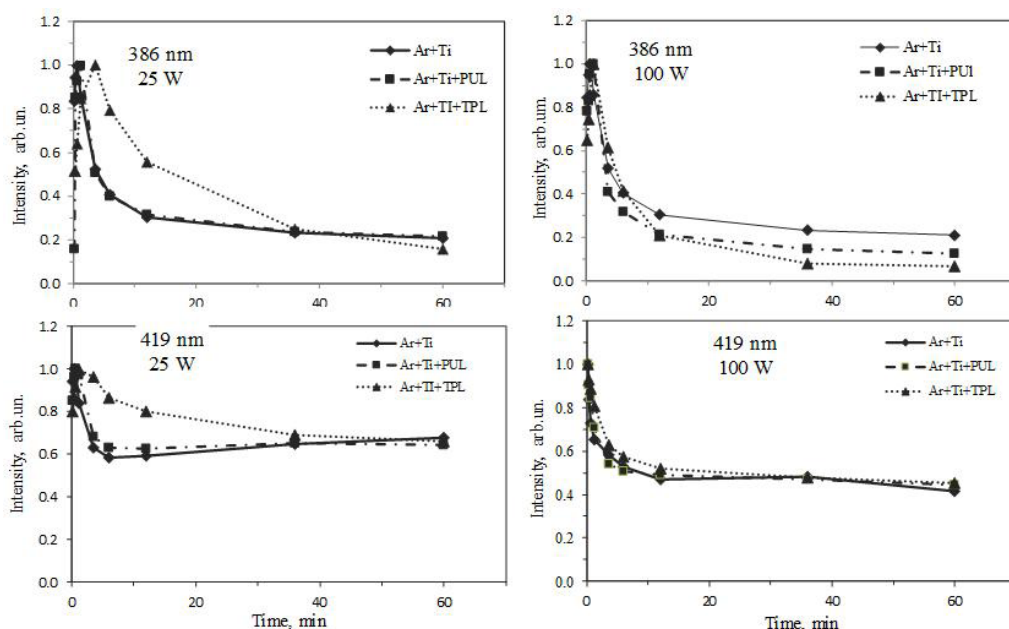
FIG. 7: Optical emission peak intensities (normalized to maximum values) of 386 and 418 nm peaks versus plasma cleaning time measured at RF plasma powers of 25 and 100 W.

reflects the variation of surface density of particles $N_{a,s}$. Thus, a decline in the peak intensity I_a to the lowest value indicates a decrease in surface density of contaminants, also to the lowest level. That relationship allows one to set up an endpoint of plasma cleaning, for example, setting the endpoint at 10% of the lowest level of a peak intensity.

B. WCA of CP Ti Surfaces Cleaned in Ar Plasma

The WCA of a chemically cleaned CP Ti coupon surface depends on ambient humidity and ranges from ~30 degrees at low humidity to ~45 degrees when humidity is ~70%. WCA decreases rapidly when coupons are exposed to 25 or 100 W Ar plasma. Approximately 3–5 s of exposure to Ar plasma reduces the contact angle to <10 degrees (Fig. 8). Exposure of coupons to 25 W Ar plasma for 20 min or longer, or exposure to 100 W Ar plasma for ~1 min or longer, reduces the contact angle to the functional detection limit of WCA, namely, values of ~1 degree ± 1 degree.

The sharp decrease of WCA after even a short exposure to mild Ar plasma is related to cleaning the outermost surfaces of the substrate. WCA, sensitive to surface roughness, is determined mainly by the geometry and chemistry of the outermost surface, as shown in Fig. 9. The kinetics of cleaning in a mild Ar plasma in a moderate vacuum (67 Pa) is influenced by various recontamination processes that are more likely to occur
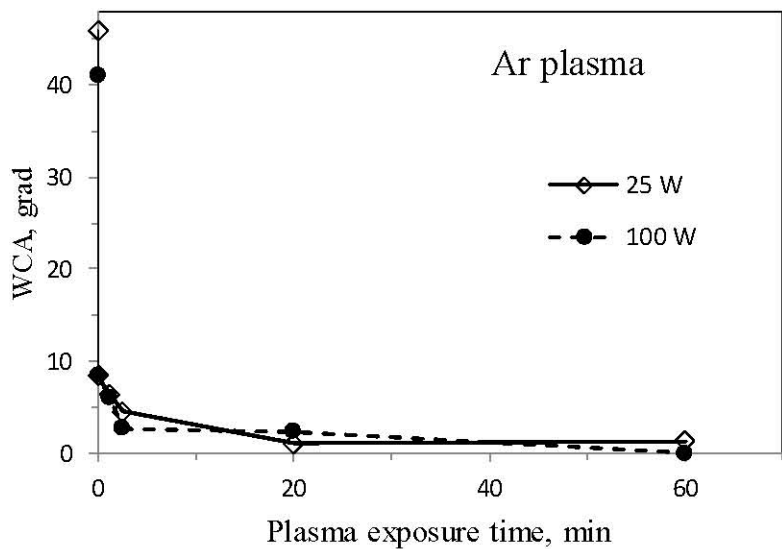
FIG. 8: WCA of CP Ti foil coupon dependence on plasma cleaning time using different power Ar plasmas. Initial WCA measurements were performed within 1 min of extracting samples from the vacuum chamber.

at the bottom of "mountains"; therefore, the top of the "mountains" gets cleaned first. Electrical field distribution near the tops could provide an additional enhancement in cleaning of those regions.

Decreased WCA on the intentionally soiled coupons indicates the removal of surface contaminants, and at a WCA of 1 ± 1 degree, most biomedical surfaces are considered cleaned and ready for medical use. However, comparing OES cleaning times with WCA time to achieve 1 ± 1 degree suggests that relying on WCA alone could result in the acceptance of parts that are not fully decontaminated.

Exposure of plasma-cleaned surfaces to ambient atmosphere (aging) recontaminates
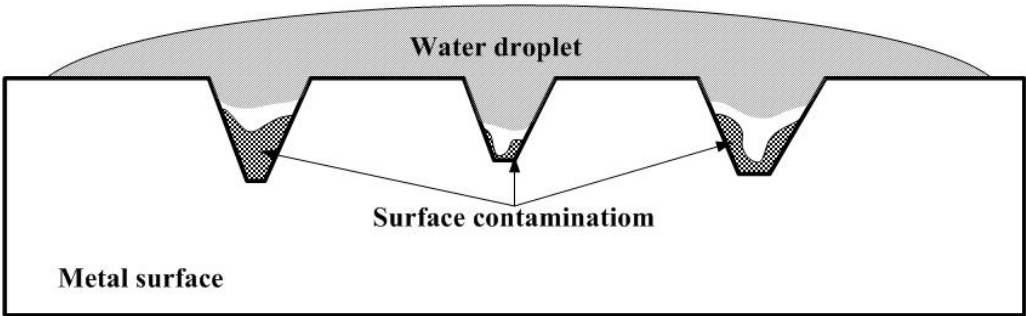
FIG. 9: Water droplet on a partially plasma-cleaned metal surface with microroughness and regions of contamination inside the trenches.
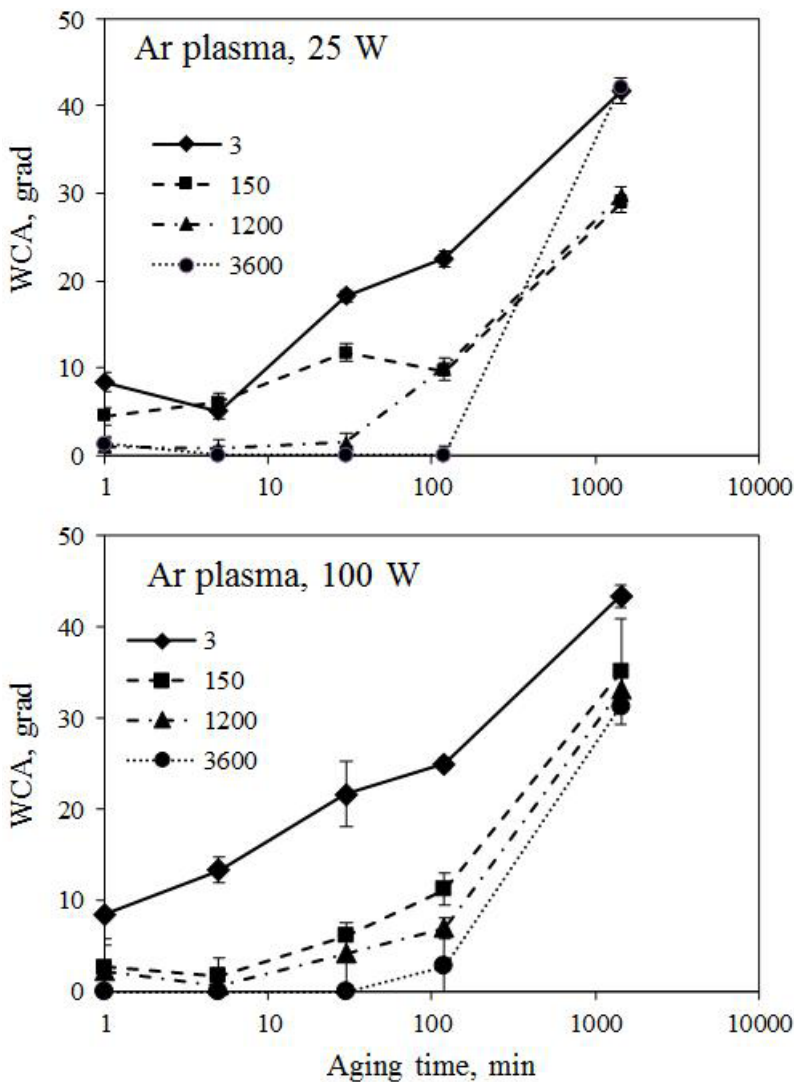
FIG. 10: WCA of CP Ti foil versus aging time (plasma posttime) after plasma cleaning.

the surfaces, creating a short time during which the materials can be assumed to remain truly clean. WCA of the cleaned coupons increases with aging time and in all cases after ~24 h reaches the values obtained before plasma cleaning (Fig. 10). Surprisingly, the recontamination rate in the ambient environment depends on plasma cleaning time. But when we consider that our data show that spectral lines in the cleaning region continue to decrease long after WCA is known to reach 1 ± 1 degree, it becomes possible to explain the dependence in the rise of WCA on plasma cleaning time. If atmospheric contamination of a surface is assumed to occur at a constant rate over time and we
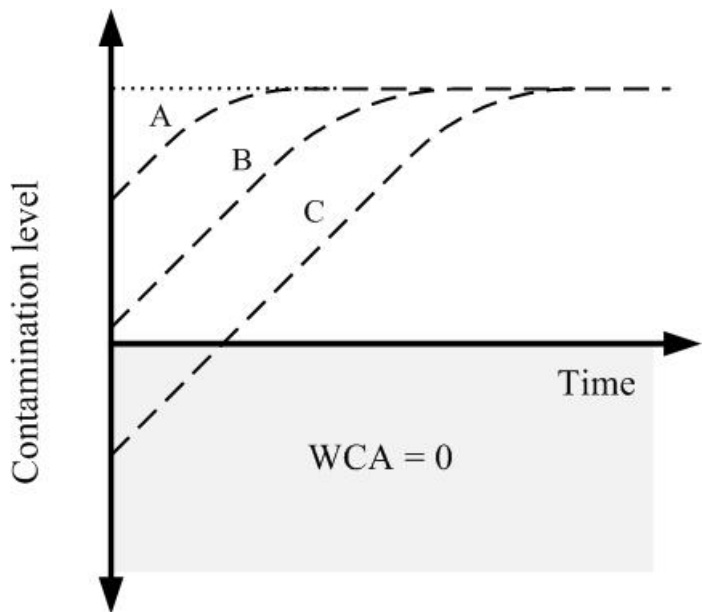
FIG. 11: Hypothetical dependence of surface-contamination level of a rough surface on time after cleaning plasma. Lines A–C represent three samples of Ti prepared with minimal, moderate, and substantial plasma cleaning, respectively. The marked area under the horizontal axis represents the conditions at which WCA = 0.

consider that a WCA of 1 ± 1 degree is not the true baseline for cleanliness of a surface, we can draw a series of lines to represent the contamination of surfaces whose baseline levels of cleanliness go to a theoretical WCA of <0 (Fig. 11). Because recontamination is constant, the slope of the lines is the same among samples, but the y intercept changes depending on the initial level of cleaning. This prediction for recontamination is in line with the data presented in Fig. 10.

Relying on only WCA as an assessment of the cleanliness of an implantable titanium or Ti alloy part may be justifiable if the part is either immediately packaged in a protective envelope with a reasonably low moisture/vapor transmission rate or the biocompatibility of the medical device is tested using surfaces that have been recontaminated in a manner similar to that of the actual marketed product. If the surface is intended for chemical modification postplasma treatment, for example, by functionalization with a SAM, recontamination over time would be expected to limit access to titanium oxide groups and would therefore decrease the uniformity of applied chemistry.

The simple test configuration presented in this work allowed for detailed analysis of the cleanliness of CP Ti. It is also apparent that the techniques applied in this study should allow for the determination of mass and constituents present in thin films built on inorganic substrates. We are currently exploring this possibility.

IV. SUMMARY AND CONCLUSION

Plasma cleaning of Titanium is an important step in the preparation of parts for various applications in medicine. XPS and Auger spectroscopy have been used to characterize the cleanliness of Ti surfaces, but those techniques are expensive, require high-vacuum systems, and are not applicable for routine control of metal-surface preparation. We show that OES can be used during plasma cleaning to track the disappearance of spectral lines related to surface contaminants on CP Ti. We have identified cleaning reference peaks at 386 and 418 nm that correspond to known surface contaminants and are reduced as a function of plasma power and cleaning time. We also demonstrate that this technique provides information beyond the "limit of detection" of contact angle, which is commonly used for assessing the endpoint cleaning of Ti surfaces. The recovery of contact angle from a WCA of 0 is delayed in samples that were cleaned with longer durations of Ar plasma, thus demonstrating that a contact angle of 0 is not an appropriate measurement to ensure that a Ti part is completely cleaned. In medical applications where robust cleaning is essential for success, OES may be an appropriate tool.

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