ANTI-FOULING STAINLESS STEEL BASED SURFACES FOR MILK HEATING PROCESSES

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ABSTRACT

One of the strategies which have been defended to reduce fouling during heat treatment in the dairy industry is to modify the surface properties of the stainless steel used in heat exchangers, in order to decrease its appetence for milk deposits. Previous studies performed in our laboratory on fouling caused by milk components on several stainless steel materials with different surface modification techniques showed the importance of specific surface properties on the type of deposit formed. One of those properties was the surface energy. In the present study, several surfaces with specific surface energies and similar surface composition were obtained by one of the most promising modification technique tested before, reactive sputtering, and were used as fouling supports in contact with a milk simulating solution under constant conditions of temperature, pH, calcium concentration and hydrodynamics. The aim of these new experiments was to quantify deposition and removal parameters, based on the influence of surface energy on the type of deposit formed.

A new dependence relation between the amount of deposit formed and the remaining deposit after cleaning with water and the surface energy of the surface, more precisely its γ^- parameter, was found.

INTRODUCTION

One of the challenges for researchers within the dairy industry is still to understand and try to minimize fouling caused by milk on processing equipment during its heat treatment. The most common type of material used in process equipment in the food industry is stainless steel and several techniques to modify its surface properties have recently been developed with the goal of reducing the build up of unwanted deposits (fouling) in dairy industry pasteurizers and sterilizers. The characterization of some of those techniques was recently published [Santos et al., 2004] and their role on fouling caused by several milk components and dairy products have also been published [Rosmaninho et al., 2001; Rosmaninho et al., 2003; Rosmaninho and Melo, 2005]. Several surface parameters are known to affect and control the fouling process, one of which is the surface energy. Previous work was carried out on the effect of surface energy on fouling with materials that not only had different surface energy but were also subject to completely different surface treatment processes (chemical composition was thus quite distinct from surface to surface). In this work, one of the most promising anti-fouling techniques previously tested, reactive sputtering was used to obtain a number of stainless steel materials with similar surface composition and morphology but variable surface energy values.

Fouling caused by calcium phosphate, the main mineral component of milk deposits (Jeurnink et al., 1996; Visser, 1999) and the role of the deposition surface energy on fouling build-up and cleaning was the aim of the present study as a way of better characterizing fouling caused by milk.

Calcium phosphate deposition and adhesion on a solid surface is the result of a competition between different types of interactions involving calcium phosphate particles, the deposition surface, the solvent and any other solute present in the system. This deposition mechanism can be divided into several steps where all the mentioned factors can be included.

The process starts with calcium phosphate particle formation in the bulk upon heating. Once at the vicinity of the surface, these particles can adhere to it following a process that is dependent on the forces established between the foulants and the surface. This process step depends on the interaction forces established between the particles and the surface, that is, on the surface properties of the particles and of the metal support. The forces that play a role in the adhesion of the calcium phosphate onto a metal heated surface are, according to van Oss (1994), the Lifshitz -Van der Waals interaction forces (LW), the electrostatic double layer interaction forces (EL), the Lewis acid/base interaction forces (AB) and the Brownian motion (Br). As a result of all these forces, van Oss divided the surface energy of a surface into four components, the electron donor (γ^-) component being the most often used characterizing component for solid surfaces (Rosmaninho et al, 2001; van Oss et al, 1997, Wu and Nancollas, 1998). After the first layer is formed on the solid surface, other particles coming from the bulk liquid adhere on top of this layer and develop a more or less structured and compacted deposit. The structure of this

deposit depends both on the structure of the first layer, which depends mainly on the surface properties, and on the particles and ions present in solution which will contribute to the growth of the deposit (precipitation/crystallization kinetics). These factors and their interactions will also determine another important characteristic of the deposit when considering a fouling phenomenon, which is its resistance to removal, more precisely the amount of deposit kept adhered to the surface after cleaning.

MATERIAL AND METHODS

Calcium Phosphate

Calcium Phosphate: Calcium phosphate deposition was performed using SMUF (Simulated Milk Ultra Filtrate), which is a water solution that simulates the mineral composition of milk. It was prepared according to Jenness and Koops (1962), pH value adjusted to 6.80 with NaOH 0.5M and kept overnight at 5ºC before use.

Surfaces and Surface Characterization

Stainless Steel Surfaces: To study the influence of the surface energy of the support on the deposition process, different surfaces with a wide range of surface energy values and similar roughness and compositions were used. All surfaces were 316 2R (bright annealed) based and were prepared by a surface modification technique called reactive sputtering coating (with Ti and N). Because it is a coating technique, all the surfaces became covered by a similar layer of TiN which makes them different mainly on their surface energy. The surfaces were named TiN 10, TiN 11, TiN 12, TiN 13, TiN 14 and TiN 15.

Cleaning Procedures: Before each deposition experiment, as well as before the determination of the surface energy of each sample, all stainless steel samples were cleaned with a commercial detergent (RBS35 from RBS Chemical Products) according to the following procedure: 1) samples were immersed in a 2.0% w/v detergent (RBS35) solution in distilled water at 65ºC for 5 min.; 2) rinsed with distilled water at 65 ºC for 5 min. and 3) rinsed with distilled water at 20ºC.

Contact Angle Measurements: Contact angle values were measured by the sessile drop method in a contact angle meter (DataPhysics OCA15 Plus) using water, formamide and α-bromonaphtalene (α-BR) as reference liquids. The contact angles were measured automatically using an image analyzing system. Contact angle measurements were performed on every stainless steel sample 24h after being cleaned.

Surface Energy Determination: Using the measured contact angle and considering the approach of van Oss (1994) it was possible to evaluate the surface characteristics of a solid according to its surface energy (γ_s). This approach considers the total surface energy of a solid or a liquid (γ^{TOT})

as the sum of an apolar Lifshitz-van der Waals component (γ^{LW}) and an acid-base polar component (γ^{AB}):

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB} \tag{1}$$

The acid-base forces are always asymmetric since they comprise the electron donating as well as the electron accepting properties of a surface. Thus the acid base component (γ^{AB}) consists of two non-additive parameters, one for the electron donor (γ^-) and one for the electron acceptor (γ^+) contribution (van Oss, 1994).

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \tag{2}$$

The total interfacial energy between phases i and j can be expressed as

$$\gamma^{TOT}_{ij} = \gamma^{LW}_i + \gamma^{LW}_j - 2\sqrt{\gamma^{LW}_i \gamma^{LW}_j} + \\ 2\left(\sqrt{\gamma^+_i \gamma^-_i} + \sqrt{\gamma^+_j \gamma^-_j} - \sqrt{\gamma^+_i \gamma^-_j} - \sqrt{\gamma^-_i \gamma^+_j}\right) \tag{3}$$

Contact angle values (θ) can be related to the total interfacial energy using simultaneously three forms of the following equation resulting from Young's equation, one for each reference liquid used

$$(1 + \cos\Theta)\gamma^{TOT}_l = \\ 2\left(\sqrt{\gamma^{LW}_s \gamma^{LW}_l} + \sqrt{\gamma^+_s \gamma^-_l} + \sqrt{\gamma^-_s \gamma^+_l}\right) \tag{4}$$

where subscripts s and l mean solid and liquid, respectively.

Experimental Equipment and Conditions

Surface Preparation by Reactive Sputtering: All of the evaluated surfaces TiN coatings were produced by reactive sputtering of a titanium (Ti) target (99.7 % purity) with an unbalanced magnetron cathode. As reaction gas, nitrogen (99,998 % N_2 volume) was used. The ratio between the process gases, argon and nitrogen was varied according to Table 1.

Table 1 Reactive sputtering coating process parameters used for producing the surfaces tested

TiN surface	Substrate Bias (V)	Ar (sccm)	N2 (sccm)	Pressure (10^{-3} mbar)
10	10	100	15	3.90
11	14	85	30	3.83
12	16	70	45	3.90
13	16	77	38	3.61
14	21	5	110	3.08
15	17	58	57	3.52

For all cases the dc sputter power was kept constant at a value of 2800 W and the sputter distance between the target and the substrates was 200 mm. During the deposition

process of TiN, the substrate was kept electrically floating. The sputter process took about 600 seconds in order to achieve a coating thickness of approximately 1 µm.

The substrates were cleaned with acetone and kimwipes papers before were mounted into the vacuum chamber, after which a plasma cleaning process followed. The rf power applied to the substrate was 500 W and the flow rate of Argon (Ar) was 80 sccm. A resulting pressure of 2.28×10^{-1} mbar was gauged. To enhance the adhesion of the final TiN coating, a pure 25 nm thick titanium (Ti) interlayer was sputtered, with sputtering parameters of 2800 W dc sputter power, 115 sccm Ar gas flow rate, 3.95×10^{-3} mbar chamber pressure during 100 sec.

Rotating Disk Apparatus: The rotating disk apparatus (Figure 1) was used to study the deposition of calcium phosphate onto a surface under controlled hydrodynamics. The apparatus is composed of a hollow cone containing heated silicone oil that can freely rotate in the SMUF solution. The solution was contained in a cylindrical thermostatted vessel whose temperature can be adjusted. The stainless steel sample used as deposition support was attached to the bottom of the heated cone by using a double-sided tape.
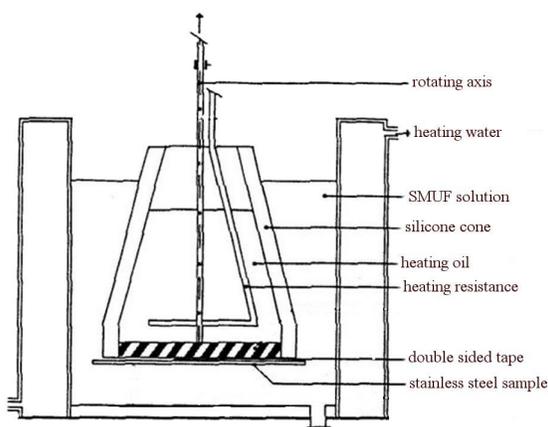

Figure 1: Scheme of rotating disk apparatus

Experimental Conditions of the Deposition Experiments: The deposition of calcium phosphate was evaluated at two different temperatures, 44° and 70°C under constant conditions of pH, temperature, calcium concentration and conductivity. This condition was one of the main differences between the present work and other work performed earlier by these authors [Rosmaninho *et al.*, 2001; Rosmaninho and Melo, 2005].The temperatures chosen were based on conclusions drawn in previous works [Rosmaninho *et al.*, 2003] which showed that different deposition behaviours were found for these temperatures, although under batch non-renewed SMUF solutions.

In this case, the SMUF solution was introduced in the thermostatted vessel of the rotating disk apparatus and its temperature was adjusted the desired temperature. When

that temperature was reached, the stainless steel sample (90 mm in diameter) was attached to the silicone cone previously heated and submersed in the solution. The sample was kept rotating at a speed of 150 rpm (laminar regime) for the desired period of time, lifted from the solution, detached from the cone, dried up in air and weighed to evaluate the amount of deposit formed. To build the deposition curve on each surface, sample were removed from solution after 15, 30, 45, 60, 120 and 240min of immersion.

The solution parameters were kept constant by constantly renewing the solution of the vessel where the deposition process was being evaluated. The pH of the solution decreased to 6,7 (WTW inolab pH level1) after the solution became turbid and kept practically constant after that point Throughout the experiments, the conductivity of the solution and the calcium concentration were approximately constants.

Deposit: The amount of deposit formed on each sample was determined by weighing the samples before and after the deposition using an analytical balance (AND GR-200).

Experimental Conditions of the Removal Experiments: The deposits formed after 240 min of deposition were submitted to removal in water at the same temperature of deposit formation. The SMUF solution was replaced by distillate water (pH 6.8 and 44ºC or 70ºC) and the cone with the sample attached was introduced in the water and started rotating at an increasing rotating speed of 165, 180, 210, 240, 270 and 300 rpm during 5 min for each one. After that, the sample was removed, dried and weighed. The amount of remaining deposit was calculated based on this last weighing.

RESULTS

Surface Characterisation by Contact Angle Analysis

Because the same modification technique was used on all the surfaces, only changing the operational parameters, the different TiN sputtered surfaces had the same surface composition although in different proportions and similar morphology, but different surface energy properties. All the surfaces were then characterized according to their surface energy in order to differentiate each one (Table 2) and at the same time evaluate the effect of the operational parameters on the surface energy of the produced surfaces. Surface energy was determined by contact angle measurements and calculated according to equation (4).

Table 2 Surface energy components for all TiN sputtered surfaces (standard deviation in brackets)

TiN surface	γ^{LW} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	γ^{TOT} (mJ/m^2)
10	43.2 (0.1)	0.7 (0.0)	55.3 (0.0)	55.7 (0.1)

11	43.4 (0.2)	0.8 (0.1)	51.6 (3.2)	56.2 (0.4)
12	43.6 (0.2)	1.3 (0.0)	23.0 (1.8)	54.3 (0.2)
13	43.4 (0.1)	1.0 (0.2)	46.2 (4.6)	56.7 (0.4)
14	43.4 (0.1)	1.3 (0.1)	18.4 (2.7)	53.2 (0.4)
15	42.8 (0.9)	1.0 (0.9)	26.0 (12.2)	53.0 (5.8)

According to van Oss (1994) and the Lewis acid-base theory, surface energy can be divided into three components, the Lifshitz-van der Waals component (γ^{LW}), the acid-base component that can be divided into an electron acceptor (γ^{+}), an electron donor component (γ^{-}) and total component resulting from the other three (γ^{TOT}). As already presented by the authors on previous work [Rosmaninho et al., 2001], the most distinguishing factor among surfaces is the electron donor component (γ^{-}) and once more that will be the characterizing factor considered along this work.

Based on Figure 2 it is possible to conclude that the surface energy, more precisely its γ^{-} component, can be directly related to the argon (Ar) and nitrogen (N) flow proportion.
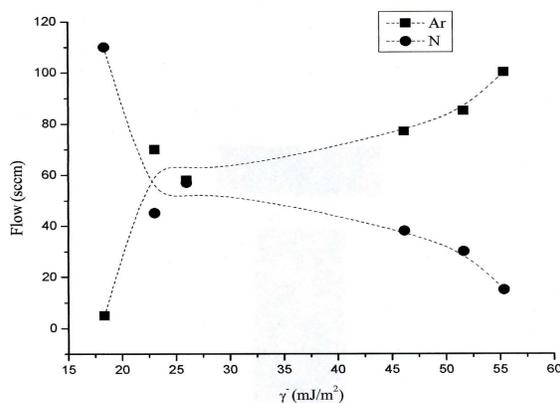

Figure 2: Relationship between the reactive sputtering production parameters (Ar and N flow rate) and the γ^{-} parameter of the surface energy of the surfaces

High γ^{-} surfaces are obtained when the combination higher flow of Ar and lower flow of N is used. This means that a high proportion of Ar/N is responsible for obtaining surfaces with high polar surface energy. Based on this relationship, it is possible to conclude that the γ^{-} parameter of the surface energy can be related to the composition of the surface. This relationship was not, however, found for the total surface energy.

Deposition Process of Calcium Phosphate on TiN Surfaces

The build up of calcium phosphate on the different surfaces was determined by weighing the deposit formed after 15, 30, 45, 60, 120 and 240 min. Figure 3 represent two characteristic deposition curves at 44ºC. It plots the amount of deposit formed against the deposition time for the surface

with the highest surface energy value (TiN10) and the lowest (TiN14).
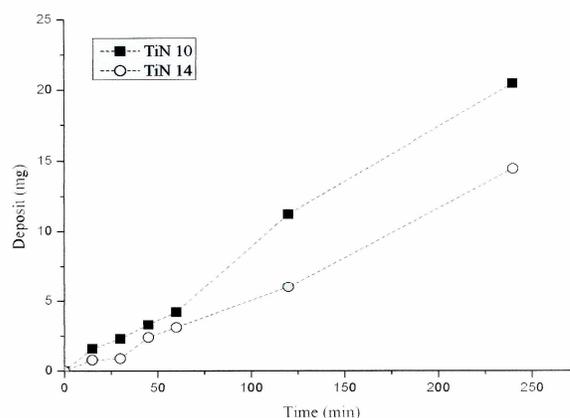

Figure 3: Deposition curves for the different TiN surfaces at 44ºC

At this temperature, the different surfaces show a similar deposition curve in the initial stages of the process, mainly during the first 60 min of contact between the surface and the solution. After that period, the deposition curve becomes differs from surface to surface, which seems to indicate that bulk properties may prevail in the deposition process at longer times.

For the same surfaces, the characteristic deposition curves of calcium phosphate at 70ºC with time are presented in Figure 4.
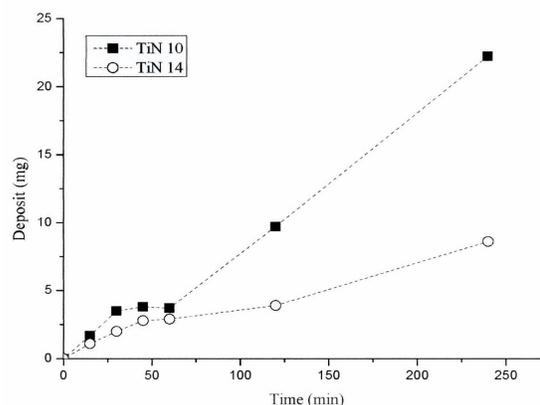

Figure 4: Deposition curves for the different TiN surfaces at 70ºC

It becomes clear that the differences between the deposition curves are much more pronounced at 70 ºC than at 44 ºC.

Based on Figure 3 and 4 it is possible to expect that the modelling of calcium phosphate deposition from solutions like SMUF on surfaces with different surface energies is a very complex process. This is due not only to the unequal affinities of the different surfaces for initial adhesion but

also to the effects they may have on the kinetics of the growing deposits at longer times.

The first deposits detected by weighing were obtained after 15 min of contact between the solution and the surface and are presented in the following figure for both temperatures studied. For all the surfaces, as could be expected, more deposit was formed at higher temperatures (70ºC). Different results were found in earlier works but in those cases the calcium concentrations were not the same at 44 and 70ºC and this probably affected the amount of deposit [Rosmaninho et al., 2003].
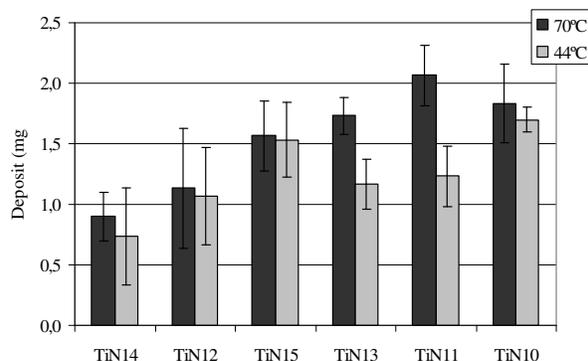

Figure 5: Deposit mass formed after 15 min of deposition which is the first mass detected at 44 and 70ºC. Surfaces are placed from left to right in an increasing order of their surface energy, more precisely their γ⁻ parameter

In the present work, the deposition was also dependent on the surface and a relationship with the γ⁻ parameter of their surface energy was found mainly for the assays at 44ºC. The trends shown in Figure 5 indicate that more deposit is initially formed on surfaces having higher γ⁻. This dependence was already found in previous works and can be related to the different affinity of the surfaces to nucleation and consequently to the combination of size and number of the first aggregates of calcium phosphate formed on the surface [Rosmaninho and Melo, 2005].
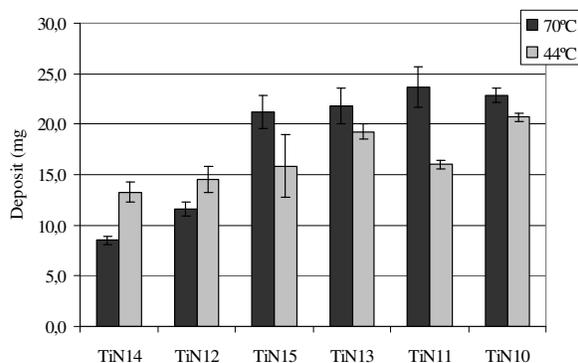

Figure 6: Deposit mass formed after 240 min of deposition (final deposit) at 44 and 70ºC. Surfaces are placed from left to right in an increasing order of their surface energy, more precisely their γ⁻ parameter

The deposition process can be divided mainly into two stages: 1) the nucleation and initial adhesion of the deposit to the surface, which can be directly related to the surface properties and 2) the development or growth of the deposit, this one being dependent on both the initial deposition layer formed and on the bulk properties, including hydrodynamics. The deposits plotted on Figure 6 were obtained after a longer period of time (240 min) and can be considered to be the result of both processes. In this work no clear effect of the temperature was found among the surfaces since in some cases (TiN 14 and TiN 12) more deposit was obtained at 44ºC than at 70 ºC while in other cases (TiN 15, TiN 13, TiN 11 and TiN 10) the opposite result was obtained. The dependence between the amount of deposit formed and the surface energy properties of the respecting surface is somehow present but not as evident as it was for the first stages. The different behaviour presented in previous plots points out to the importance of the surface at initial stages of deposition and the importance of the flow or bulk conditions for later stages.

Cleaning Properties of TiN Surfaces after Calcium Phosphate Deposition

The calcium phosphate deposits presented in Figure 6 were submitted to removal experiments at the temperature of deposit formation. Figure 7 plots the remaining deposit mass after removal with water for the different TiN surfaces. This information is very important when considering the cleaning of deposits formed on heat exchangers, since it corresponds to the end of the first step of the cleaning process.

Although more deposit was formed at 70ºC than at 44ºC, more deposit remained in this last case for all the surfaces. The fact that the removal experiment was performed at different temperatures may have affected this result since the dissolution of calcium phosphate is different at 70 and 44ºC. However, after mild cleaning with detergent as explained in "Cleaning Procedures", the surfaces which were submitted to deposition at 70ºC were almost impossible to clean since a persistent residue was always found (data not presented). This may indicate that even in smaller amount, the deposits formed at higher temperatures are more strongly adhered to the surfaces and consequently more difficult to be completely clean.
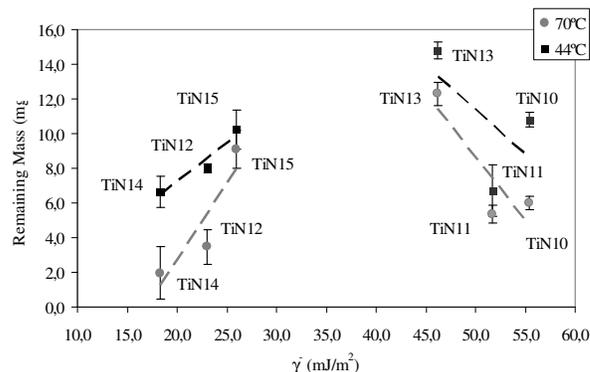
Figure 7: Remaining deposit mass after removal experiments with water at 44 and 70 ºC (for deposits formed at 44 and 70ºC respectively)

The results here presented emphasize the fact that the remaining deposit after cleaning with water depends to a certain degree on the surface energy of the support. It looks as though the mass of the remaining deposit is smaller either for materials with low or high surface energy, whereas a maximum of residual deposit is found on surfaces having a γ^- parameter somewhere between 30 and 45 mJ/m^2. This result needs confirmation and a deeper analysis, in order to seek for an explanation which is not clear at the moment.

CONCLUSIONS

The deposition process of calcium phosphate from a complex solution (SMUF) on TiN sputtered surfaces can be characterized by:

1) Having different deposition curves for surfaces having different surface energy parameters;

2) Under similar conditions, more deposit is formed at 70ºC than at 44ºC for all the surfaces at initial stages of deposition; however, for longer deposition times, this behaviour is only found on surfaces with higher γ^- ;

3) Having an intriguing relation between the residual deposit mass after cleaning (with water at the same temperature of deposit formation) and the γ^- of the surface used. In general, after cleaning less deposit remained on the surfaces with the highest and the lowest γ^-. A probable maximum of residual deposit seems to exist on surfaces having a γ^- parameter somewhere between 30 and 45 mJ/m^2.

ACKNOWLEDGEMENT

NOMENCLATURE

SMUF	Simulated Milk Ultra Filtrate	
TiN	Titanium-nitrogen	
γ	Surface energy	[mJ/m^2]
γ^{LW}	Lifshitz-van der Waals component	[mJ/m^2]
γ^{AB}	Acid-base component	[mJ/m^2]
γ^-	Electron donor	[mJ/m^2]
γ^+	Electron acceptor	[mJ/m^2]
θ	contact angle values	[º]
sccm	standard cubic centimetre	
Bias	voltage at the substrate	[V]

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