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"Surface Treatments for Industrial Applications"

UPGRADING OF SILVER EDIBLE COATINGS ON CARDAMOM SEEDS

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GENERAL CONTENT

ABSTRACT

In this work, Cardamom seeds were coated with silver by the Magnetron Sputtering technique. Twenty (20) processes were tested in different ways with wet and dry treatments and then sputtered. The wet treatment was made in order to reduce the size of a sugar buffer coating of the seeds, while surface treatments were applied to improve the aspect of the seeds. The parameters of deposition were 0,2 and 0,15 A of current for the cathode, $5x10^{-3}$ mbar pressure of work and the other parameters depend on the samples. The aim of the work was based on obtaining cardamom seeds with a silver coating that has silver appearance and small size. The ideal aspect of the seeds and their sizes are to be similar to the usual Cardamom seeds on the market. For this reason the seeds had a sugar and water layer that avoid degassing from the seeds. A dissolutions of this covering was made to reduce their sizes (wet process) and a dry tumbling treatment was applied before deposition process to improve the coating.

INTRODUCTION

India is a very diverse country with a very rich gastronomy. In Indian culture, the consumption of spices and seeds is the key for the aroma and flavor of this spectacular cuisine. Cardamom, also called "the queen of spices", is highly used in food and drinks as well as a medicine because of its several good effects on digestion, teeth infections, pulmonary diseases and so on.

Other important elements of Indian gastronomy are silver and gold. These precious metals are incorporated since ancient times, mainly as a luxury seasoning and as a tribute for guests. Silver has been present in the antique Indian medical books (Ayurvedic) due to the antibiotic and antimycotic properties. Also, silver is considered an important astringent. At the present time, medical research has demonstrated good antiseptic effects of silver in the human body when right doses are administrated.

Cardamom and Silver are combined, as healthy elements, in common Indian snacks, where indeed cardamom seeds are covered with silver. In order to unite these two healthy elements, cardamom seeds covered with silver is a common snack in India. However, the covering is produced through the manufacture of Varak or Vark, which is a very thin silver layer made by hand, smashing with a hammer several sheets of material at the same time until the layer has the thickness of some microns. This manufacturing normally has its consequences over people who work in this field. The most relevant consequence is the "Argyria" which is a skin disease produced by long exposure to silver.

With the intention of avoiding the manufacturing process of Varak, another technique was experimented during this work: the Magnetron Sputtering technique to produce a silver coating onto cardamom seeds. In this way, it should be possible to produce edible coated seeds without direct contact with silver and consequent contamination.

William Grove reported the phenomena of sputtering in 1852 while studying the glow discharge in a plasma. He made some experiments with deposition on a silver surface but he was more interested on the plasma phenomenology. The deposition of materials inside the discharge tubes was consider at the time, an undesired effect of the process. Another scientists as Faraday, Plucker and Wright noticed the deposition in vacuum tubes while studying plasma, but Wright was the first one to write a characterization of vacuum deposited films. Nowadays, sputtering is a widely used technique for several applications such as hardened coatings, decorative thin films, antireflective coatings, and so on.

During the sputtering process, atoms in a target (in this case silver) are bombarded with ions of a plasma and ejected from it. The atoms of the target then, are condensed over the substrate (in this case Cardamom seeds). One of the most used techniques is the magnetron sputtering, in which a magnet disposition is used in order to accelerate the process by the confinement of electrons near the target. This confinement allows to increase the ion current density at the target.

In the aim of this work, several silver depositions were made to Cardamom seeds. Dry (physical) and wet (chemical) treatments were applied in order to improve the surface of the seeds and to change the sizes of the seeds, respectively. The main difficulty to coat Cardamom seeds is degassing of essential oil since color tarnishing is produced. For this reason, a sugar covering was applied to the seeds in order to have a buffer layer between the seed and the silver coating that works as diffusion barrier. The size of the seeds was reduced to obtain silver, edible coatings on Cardamom seeds similar to the ones in the market. Some of the deposition parameters used, were obtained in a previous research in the framework of the master. Finally, small, brilliant, and silver seeds with flat surfaces were obtained.

CHAPTER 1

SILVER IN THE INDIAN GASTRONOMY

India is a territory located in the Asian continent and represents one of the most important and antiques cultures in the world. India is the second most populated country in the world, holds more than 1.300 million people in its borders and it is the seventh largest country as far as territory is concerned. Nowadays India is considered a country that brings stability to the region, especially for Bangladesh, Pakistan, Nepal and Sri Lanka.

To put ourselves in context, India is ten (10) times bigger than Italy with twenty two (22) times the amount of people. This country represents one of the most important economies in the world and agriculture products represents 13% of its total exportations. India is an extremely diverse country in religion, languages, nature and culture with its gastronomy being a great example of it.

1.1 Indian gastronomy

The Indian cuisine is based on several ways of cooking with a large variety of ingredients. The most characteristic elements are the amount of herbs, condiments and spices. The Indian gastronomy is so diverse that there are different types of plates and food depending on the region such as North, South, East and West. Also fusions with other cuisines such as Malaysian-India, Indian-Singaporean, Indian-Chinese are very popular all around the globe.

The diversity of gastronomy is based in desserts, drinks, plates and even habits in the table. The majority of Indian flavors are linked to the use of spices and a variety of vegetables. For Indian food it is very important not only the taste of the food, but the aroma, of which principal sources are spices.

1.1.1 Spices

Indian spices were the most important element in the commercial trade between India and Europe since XIV century. Even today, India represent the second country exporter of spices in the world. Some of the most known spices are pepper (also named king of spices), cumin, cinnamon, cloves, garlic, ginger and cardamom. Spices are produced in certain regions depending on the weather and can be sold in different presentations as chopped, whole, covered, etc.

1.1.2 Cardamom

Cardamom plants (*Elettaria cardamomum*) are usually less than three (3) meters tall. This plant takes approximately three (3) years to bear fruits and can be productive from four (4) to six (6) years before its yield decreases. Cardamom, also named queen of spices, is one of the most expensive spices in the world, along with saffron and vanilla.

Two types of Cardamom exist: green and black. They can be easily recognizable by their sizes (Figure 1.1). Green Cardamom is the most common and it is smaller than the black one. Cardamom is native of India, Nepal, Indonesia, and Bhutan; but, the biggest producer of Cardamom in the world is Guatemala. Take in consideration that Guatemala only produces green Cardamom while India produces both types.

Figure 1.1: Black and green Cardamom.

The Middle East, South Asia, Southeast Asia and Europe are the most consuming Cardamom regions, but the biggest importer is Saudi Arabia. In 2010 Saudi Arabia imported 36% of total Cardamom imports, followed by Egypt with 19% (Figure 1.2).

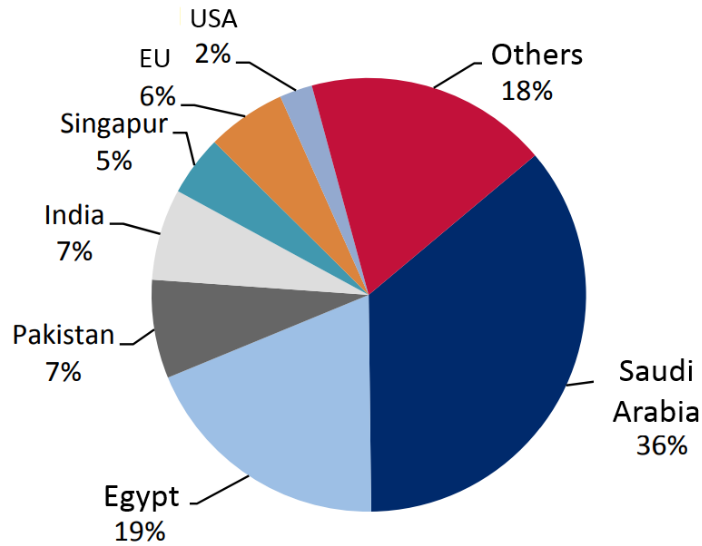


Figure 1.2: Cardamom world importers (2010) (USAID-ACCESO, 2011).

In the European Union (EU), the most important Cardamom importers by 2010 (USAID-ACCESO, 2011) were Germany, Netherlands and United Kingdom. By tradition, United Kingdom is the biggest importer because Cardamom is popular inside the Asian community in that country. The majority of Cardamom imports to the EU comes from Guatemala and India. In Europe, Cardamom has become an important ingredient for preparation of desserts and bakery products.

Cardamom is a sheath with its seeds inside, they have a transversal section with a triangle form (Gage, 1908) (see Figure 1.3). The earliest reference to this spice dates back to 2.000 B.C in a clay table where was indicated that Cardamom was used in soups and bread. In Indian medicine books (Ayurvedic), Cardamom is used to have a good breath and to treat stomach and urinary diseases (Gage, 1908). Even today, Cardamom seeds (*Elaichi* in Indian) are widely used with medical purposes and it is commonly chewed for good breath and buccal disorders. It can be highlighted, that Indian Cardamom seeds could be characterized as the most aromatic, while Sri Lanka's seeds are the largest ones.

Taking in consideration that Cardamom is an unparalleled and tasteful spice used in desserts, foods, coffee and tea, it is important to mention that it is also expensive. Because of its cost, some people try to substitute it on the market with another spices like cinnamon and nutmeg.

Figure 1.3: Cardamom seeds.

The price of the Cardamom depends on several criteria, such as size, color, dry method, if it has been whitening or not, proportion of external matter and origin of the product. The highest price of Cardamom was registered in July of 2010 when a ton costed approximately 30.000 euros (USAID-ACCESO, 2011).

1.1.3 Varak

Varak is a very thin, fragile and delicate handmade leaf of metal that cannot be touched with hands. Varak or Vark is made by smashing a piece of metal covered with paper until the layer is as thin as a few microns approximately. The metals are usually gold and silver in high purity.

In Indian gastronomy, presentation of food is one of the most important elements. Covering food with gold and silver is a common practice to decorate plates (see Figure 1.4). Also, in the Indian culture, it is well known that eating silver in small quantities is good for health because of its antibiotic and digestive properties. Another reason why Varak is important in the Indian culture is because it represents a sign of prosperity.

Figure 1.4: Varak in several dishes.

The construction of Varak is a very controversial theme. Even though, manufacturers of Varak say it is a vegan product, there are some myths about the craft elaboration of silver sheets. The paper used to smash the silver is made by skin of animals as cows and pigs. This paper is made putting the animal skin in a bath from ten (10) to fifteen (15) days when the epidermal layer is removed from the outer skin and introduced into a chemical solution to make it softer. At present, several companies has changed their materials to German sheets made of butter, in order to use non-animal products for Vark (Figure 1.5).

Figure 1.5: Varak in the commercial presentation.

A general problem with production of Varak is the amount of impurities present in the silver leaves. More than 10 % of Varak sheets are contaminated with aluminum. This is an important problem because consumption of another metal can produce intoxication.

1.2 Antibiotic properties of silver

Silver, is the 68th most abundant element on Earth. It can be found in its pure form and it is the second most malleable and ductile metal on land surface. Its chemical symbol is Ag and its atomic number is 47. Silver is usually a very attractive material because of its reflective capability. On the other hand, silver was the third metal that human could use in daily life, so the importance in cultures and history is enormous for several civilizations like Indian, Greek, Chinese and so on (Graziani, 2012).

In 400 B.C Hippocrates, who was a doctor in Greece, documented for the first time the antimicrobial effectiveness of silver. He described that silver can be used as a sterilizer for water and containers for food as well as treating wounds. Phoenicians and Chinese also used silver when they realized that water and food last longer before decomposition, so in this way they prevented digestive infections (Morones et al., 2013).

After the discovery of the penicillin 1929 and its production in large quantities since 1942, the use of silver as antibiotic was reduced radically. Nowadays, with the resistance of pathogenic bacteria to the antibiotic has become necessary to explore again silver antimicrobial properties. Several studies have been made in order to discover the mechanism of its bactericidal action. In some cases it has been possible to increase the effects of another antibiotics in a factor of 10 or even 1000. Silver can attack bacteria that are resistant to antibiotics and also work together with another antibiotics to potentiate their effectiveness. Some studies are also trying to demonstrate that silver can prevent the reproducibility of cancer and HIV cells (Morones et al., 2013).

Even though the good properties of silver as an antimicrobial agent, excessive consumption produces a skin disease called Argyria. Argyria is an affection that turns the skin of a person into a blueish color, from where comes the relation with the term "blue blood". Argyria is very common between people that make Varak because of direct contact with their skin during manufacturing. It is important to mention that this affection cannot be cured (M. As et al., 2005).

1.3 Silver coating in Cardamom

Silver coating in Cardamom seeds are usually done by a method using Vark. Silver has no taste but a shining appearance that is very attractive in the Indian culture.

It is a common snack normally sold as can be seen in Figure 1.6. Companies make Varak in an industrial form and cover the Cardamom seeds. Normal presentation can cost 10 € for a package of approximately 10 grams, depending on the company.

Figure 1.6: Usual packing of Cardamom seeds covered with silver.

CHAPTER 2

PREPARATION AND DEPOSITION TECHNIQUE FOR EDIBLE SEEDS

Cardamom seeds available were covered with a sugar and water layer of approximately 1 mm (Figure 2.1) in order to avoid degassing or diffusion of its essential oil. Degassing does not allow adhesion of silver coating to the seeds. Some seeds could be attached to another. The sizes of the seeds were diverse, but can be estimated to 4,5 mm diameter.

Different treatments were necessary to reduce the thickness of the caramel covering of the seeds and to improve their surface. In this way, silver coated seeds will be similar to the usual silvered seeds existing in the market.

Figure 2.1: Cardamom seeds with sugar cover.

2.1 Chemical surface treatment

A chemical treatment for the seeds was needed in order to reduce the size of the seeds. For this procedure, the seeds were introduced in a solution of ethyl alcohol (ethanol) and water at 50% (Figure 2.2). This concentration was chosen due to the aggressive dissolution of the seeds using only water, taking in consideration that the sugar covering cannot dissolve in alcohol.

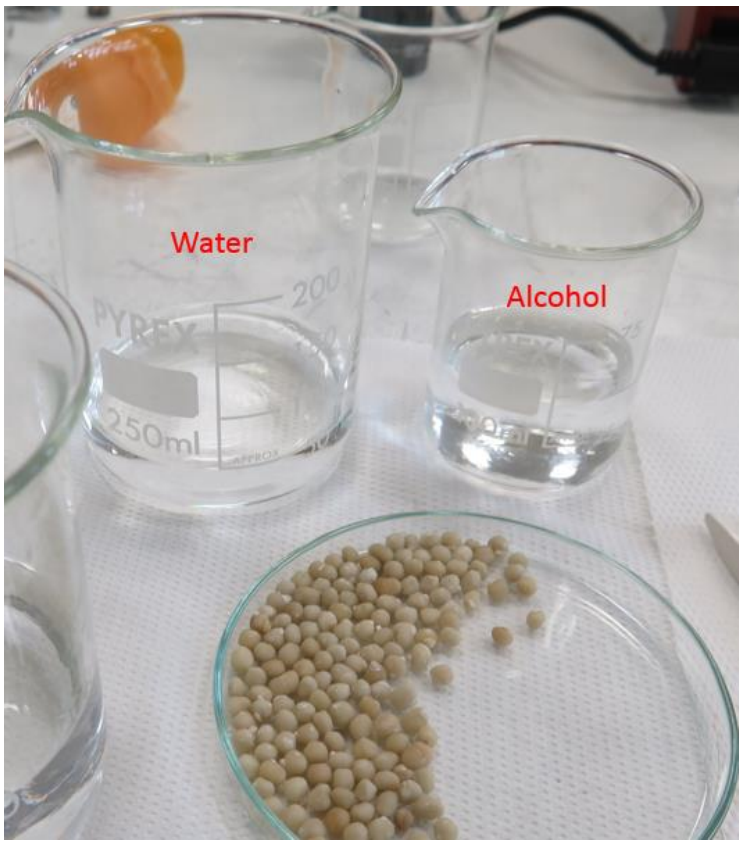


Figure 2.2: Chemical preparation to reduce the size of the seeds.

The dissolution was made during different times in order to obtain different seeds sizes. Dissolution times used were: 3 minutes, 5 minutes, 7 minutes, 8.5 minutes and 10 minutes. After dissolution, the seeds were immersed only in alcohol to eliminate all the water in them. This last wash is done preferably two or three times.

2.2 Physical surface treatment

The physical treatment was made with the purpose of to not change the size of the seeds, but to smooth their surfaces. This modification in the seeds surfaces is due only to the contact among each other, this contact along with repetitive movements improve the seeds surfaces. The movement can also be done with some other materials that accelerate the process such as sugar. The physical treatment consists in putting the seeds in a tumbler machine.

2.2.1 Tumble finishing

In order to eliminate sharp edges of a surface, it is possible to use different methods. One of them is polishing, which can be a wet or dry process. During the chemical polishing a reaction takes place and eliminates part of the surface of the material. In physical polishing, it is necessary a rubbing process to produce a smooth surface. In several cases, the polishing material is the same material as the one that needs polishing.

This type of procedure is highly common for polishing stones. Many of them are introduced in a recipient and put into a machine that generates periodic and continuous movement. In this way, the friction between the stones reduce the defects on their surfaces.

The main advantage of this technique is that it is possible to avoid the exposure of the material to another one, so there is no contamination depending on how the process is done. The tumbling process can be done introducing a liquid lubricant or solid material with the material to accelerate the process. For this reason, during this work the surface of Cardamom seeds was smoothed with this technique in some cases with sugar as an accelerating material.

The preparation of the seeds during this work, included a tumbler machine that produces rotational movements in different directions. A tumbler machine is commonly used to mix powder and liquids homogeneously. The velocity of rotation can be set up by the user. The seeds were introduced in a plastic recipient (Figure 2.3 a) and fixed in the tumbler machine (Figure 2.3 b) with rubber suspenders.

(a) (b)

Figure 2.3: (a) Seeds in plastic recipient. (b) Tumbler machine.

The main purpose of this technique is to use friction between the seeds to smooth their surfaces. In this way, the seeds do not suffer for any treatment that may change the surface in a strong or aggressive manner that could lead to change in their chemical composition. Usually the treatment lasts hours or even days, depending on the state of the seeds or the desired purpose.

The physical treatment or tumbling can be made before or after the deposition process. In this case, it was done in different conditions in order to understand the change it produces on the surfaces of the Cardamom seeds. The seeds were put into a tumbler inside a recipient with several holdings to make sure they do not fall during the process. The velocity of the tumbling was 52 turns per minute.

2.3 Physical vapor deposition (PVD)

The physical vapor deposition (PVD) is a group of processes in which a material is converted in its vapor phase and is condensed above the substrate surface. These techniques are often used because of the variety of materials that can be deposited as metals, alloys, ceramics, inorganic compounds, and even some polymers. The substrate can be heavy metals, glass and plastic. Applications of the PVD include: decorative coverings in plastic or metallic pieces, antireflective, and hardening coatings.

In general, the deposition techniques induce modifications in the surface of the chosen material or substrate, with the deposited material. In this process, properties of the surface such as mechanical, optical and conductive properties are modified.

PVD technology has been one of the most important techniques for high quality coatings in the last forty (40) years. Different types of PVD exist depending on the evaporation process involved: thermal evaporation or ionic evaporation. Some of the thermal processes are: vacuum evaporation, pulsed laser deposition, and molecular beam epitaxy. Some of the ionic evaporation are: Ion plating, sputtering, etc.

The sputtering technique is a process of evaporation or ionic evaporation, consisting on bombarding energetic ions in a material named target until evaporation of these atoms is reached. The target must be in a negative potential, in order to attract ions, and it also plays the role of cathode. Positive ions of neutral gases as Argon, bombard the surface of the target. This exchange of energy produces an ejection of atoms of the target. These ejected atoms are condensate on the substrate creating a thin film. The substrate is connected to ground as it is shown in Figure 2.4.

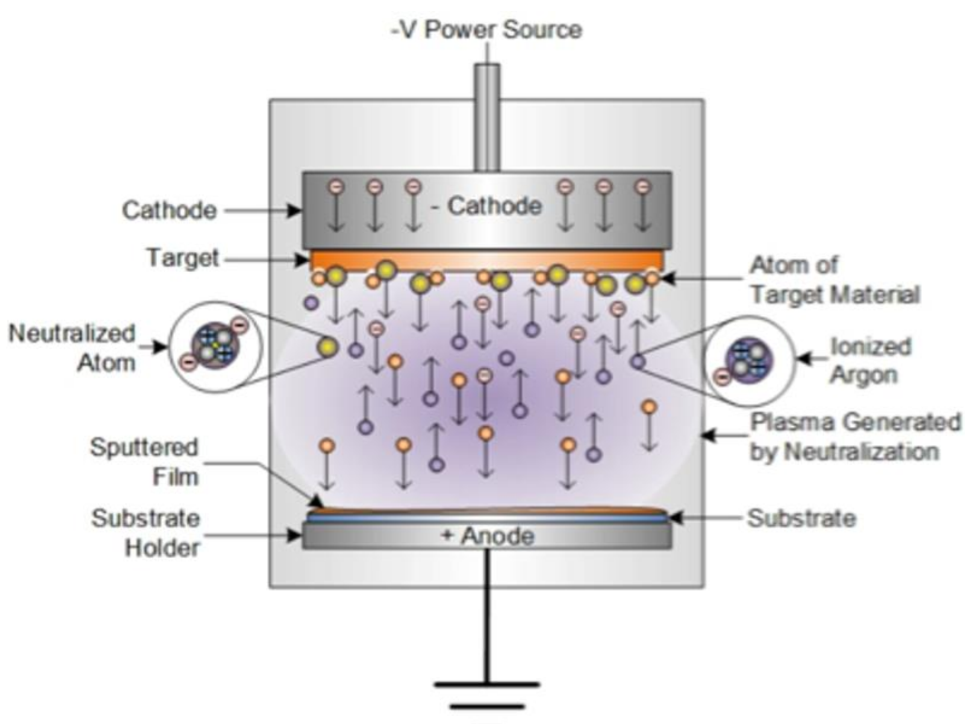


Figure 2.4: Diagram of the sputtering process.

In Figure 2.4, a diagram of the sputtering process can be observed. The difference of potential induces Argon atoms to move freely and collision each other, taking away electrons. The movements of the charged particles can be described as Lorentz forces acting due to an electric and magnetic field. These particles acquire enough kinetic energy to produce a plasma that strongly depends on the difference of potential (to which the particles are subjected) and the amount of particles present in the chamber (Argon pressure). It is necessary that the plasma remains stable through the self-sustained discharge.

Plasma is the fourth state of matter, constituted by ionized gas in which there is not electromagnetic equilibrium. During PVD processes, plasma is produced by introducing Argon gas to a vacuum chamber and applying a difference of potential. This potential excites the atoms that start to collide between each other. During this collisions atoms are ionized and this allows electricity to be conducted, therefore, plasma is a good electrical conductor.

Furthermore, Argon plasma (Argon ions) hits the surface of the cathode (target) with enough energy to rip off atoms of the target. When the target material is knocked by Argon ions, they transfer their energy to all the conforming atoms and produce a cascade collision. These multiple collisions make some atoms of the target acquire enough energy to abandon the surface.

Several phenomena take place during the target bombarding as the emission of secondary electrons and the implantation of an Argon ion into the target material (Figure 2.5). The secondary electrons contribute with the self-sustained regime of plasma.

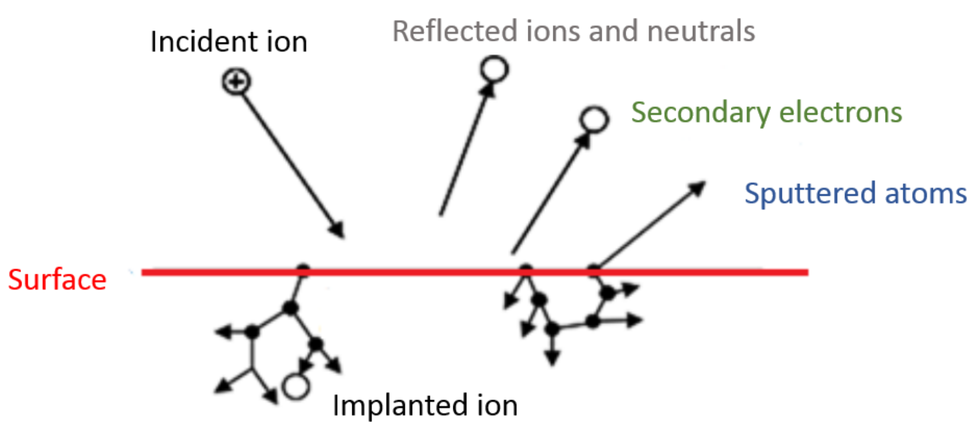


Figure 2.5: Phenomena during the target bombarding.

When kinetic energy of the incident particles exceeds the binding energy of the target solid atoms, changes occur in the target structure. With energies higher than 4H, where H is the sublimation heat of the target material, there is an increase of the ejected atoms (sputtered atoms). Those atoms go to the substrate and condensate over it. During this process, the thin film takes place growing in the substrate at a specific deposition rate and an efficiency (S) given by:

$$S = \frac{Removed\ atoms}{Incident\ ions}$$

The efficiency or sputter yield of the process strongly depends on: the energy and angle of incident ions, the target material, and its structure. This quantity refers to the target erosion velocity. Transfer of momentum and conservation of energy play a very important role in this process. It is because of these phenomena that atoms of the target can be ejected from its structure.

On the other hand, several parameters are involved in the sputtering quality process including the potential applied to the cathode, the pressure of the working gas, the substrate temperature and the distance between target and substrate.

An advantage of this deposition technique is the uniformity of the plasma above the sample, which allows a homogeneous target sublimation. There are different types of sputtering techniques, such as: ion beam, reactive, ion assisted, among others. Even with the several techniques existing, it is very difficult to reach high deposition rates, then, to solve this problem it is possible to use the magnetron sputtering technique.

2.3.2 Magnetron sputtering

John Chapin used the magnetron sputtering technique for the first time in 1970. It consists on bombarding energetic ions on the target which is confined by a set of magnets responsible of creating an electromagnetic field (Figure 2.6). The magnetic field increases the amount of ions hitting the target surface due to the Lorentz force, so the process of ejection atoms from target is faster.

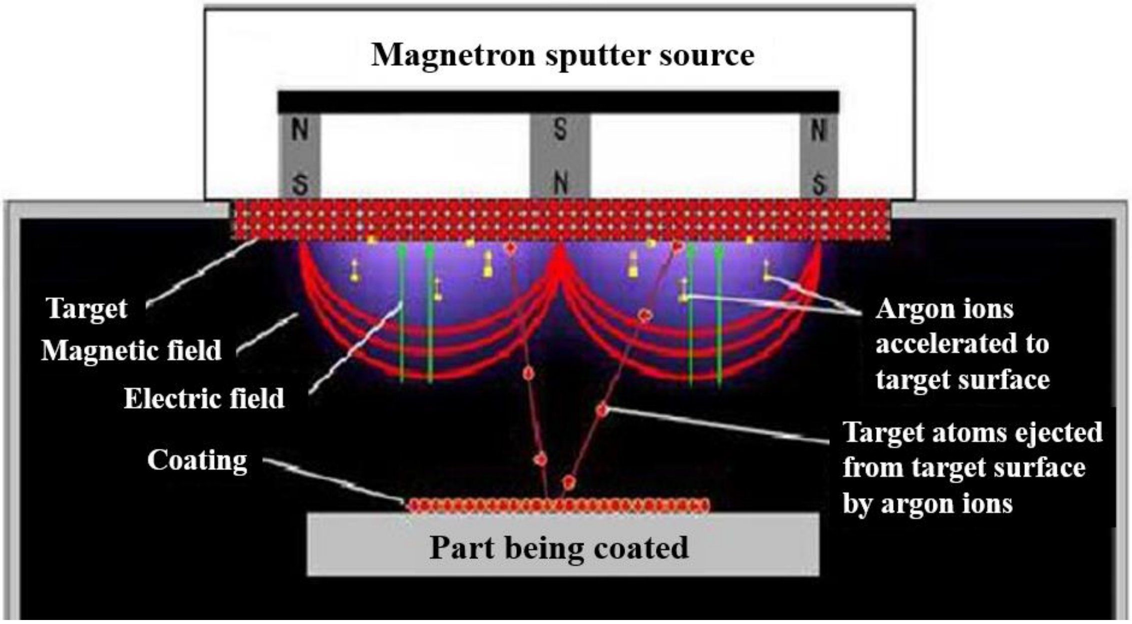


Figure 2.6: Scheme of the magnetron sputtering process.

The magnetic field produced during the process by the magnetron is designed as seen in Figure 2.7. This magnetron has two cylindrical magnets that generate a magnetic trap for plasma in order to increase the number of atoms ejected from the target.

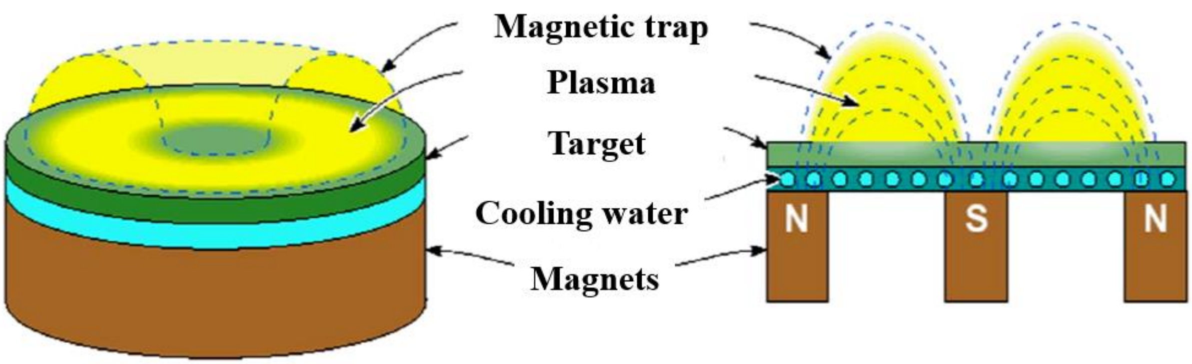


Figure 2.7: Scheme of magnetron working.

Into the magnetic trap, electrons make cycloid motions due to the interaction with the electromagnetic field. These motions increase the plasma density and consequently increase the sputtering rate. It is necessary that the working pressure to be low, in this way the sputtered atoms can travel through the plasma to the sample without collisions.

Collisions between plasma ions and atoms of the target produce an inevitable increase of the target temperature. In this sense, a cooling system (usually water flux) is needed to considerably reduce magnets temperature in order to avoid the magnets to reach Curie temperature. At this temperature, magnets lose their magnetic properties.

2.4 Scanning electronic microscopy

The Scanning Electronic Microscope (SEM) was developed by Manfred von Ardenne in 1937 and consist in a device that scans a surface with an electron beam and analyzes the emitted particles. This type of microscope uses an electron beam instead of a light beam such as the optical microscope. Usually, it is used in several fields of research as: Biology, Material Science, Medicine, and many others. One of the most important advantages of this analyzing technique is the fact that the image can be zoomed more than 2000 times with high resolution.

The functioning system is schematized in the Figure 2.8. The electron gun produces an electron beam that is confined with several instruments such as the magnetic lens. Two detectors are included in the scheme: backscattered electron and a secondary electron detector. Even though the x-ray detector is not included in the scheme, in the SEM available is present.

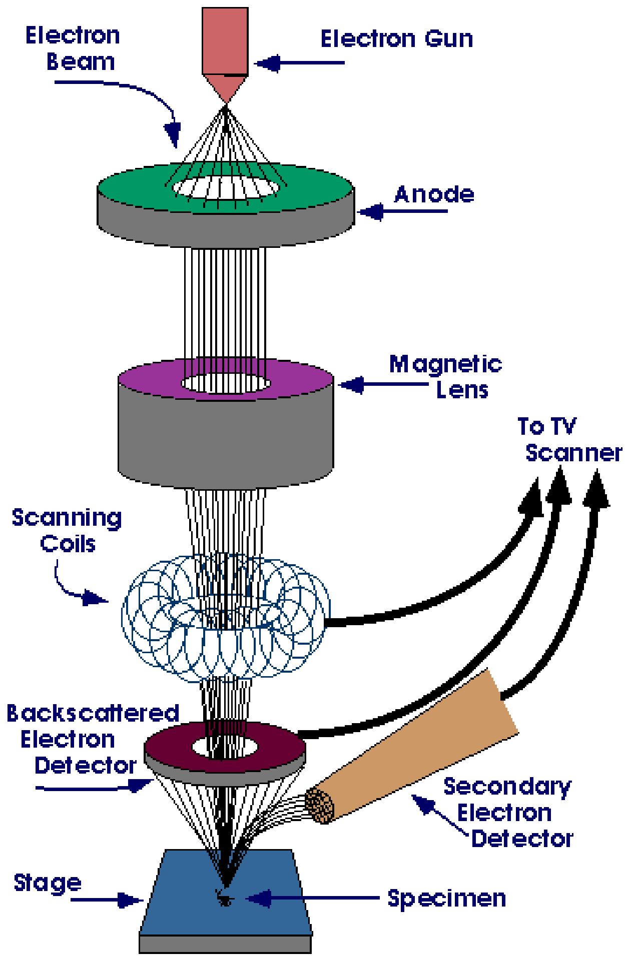


Figure 2.8: SEM inside working system.

With this instrument, the sample to analyze is bombarded with an electron beam and several interactions are produced between electrons and atoms that conform the sample. Interactions can have an elastic or inelastic origin. The most important elastic interaction is backscattering electrons in which electrons change their trajectories. The inelastic interactions can be: Auger electrons, secondary electrons emission, characteristics x-rays, bremsstrahlung, etc.

The construction of images are done with the secondary electron emission. These electrons come from the scattering of the valence electrons of the atoms that conform the sample when are bombarded with the electron beam. Another important analysis that is possible to do with this microscope is the energy dispersive x-ray spectroscopy (EDS) in which the characteristic x-ray emitted are detected and an energy spectrum is produced to identify the chemical elements present in the sample.

During this work, both SEM and EDS analysis were made in order to observe the silver coating in the cardamom seeds, measure its thickness, and know its chemical composition. The SEM is a Philips XL30 which has the capability to produce an electron beam with a potential between 5 and 30 kV. The characteristics x-rays are acquired with a Bruker silicon detector and it is possible to make a spectrographic analysis of the composition of the sample. The SEM also includes a pumping system with a rotary and a turbomolecular pump to produce vacuum inside the chamber. This system can be seen in the Figure 2.9.

Figure 2.9: Scanning electron microscope.

2.5 Profilometer

The profilometer is an instrument used for measuring thickness or mapping a thin surface. This tool electromechanically moves a diamond tip over the sample and it is able to measure differences in thickness in the order of the hundreds of nanometers. With this movement, the tip of the profilometer touches the surface of the sample (it is needed the sample to be flat). For this reason, quartz samples are commonly used to measure thickness of thin films.

During this work, a Veeco profilometer was available, model Dektak 8 as can be seen in Figure 2.10. The software of the profilometer allowed us to change length of measurement, time and several parameters in order to measure thickness very accurately.

Figure 2.10: Profilometer.

CHAPTER 3

EXPERIMENTAL PROCEDURE

The experimental procedure was based on depositing cardamom seeds using a vacuum system joined to the magnetron sputtering deposition technique. The elaboration of the silver coating with the sputtering technique can avoid the Varak craft manufacturing that includes hammering sheets of silver several times until the film thickness is reduced to a few microns. On the other hand, it is well known that Varak can contain impurities as aluminum that can be dangerous for health.

Another advantage of this procedure is the simplicity of the process and the reproducibility. In this way, it is possible to produce cardamom seeds with silver coating in large quantities. For this work, Cardamom seeds with a sugar covering were available to reproduce several samples in order to optimize the deposition process.

3.1 Vacuum system

The system used during this work can be represented with a diagram in Figure 3.1. The system is composed by a vacuum chamber, valves, a lifting machine (to open the upper part of the chamber), a control panel, a power supply, and other instruments that make possible and controllable the sputtering process. An Argon cylinder is available to insert the gas into the chamber and produce the plasma. In the diagram, the order of some instruments is illustrated.

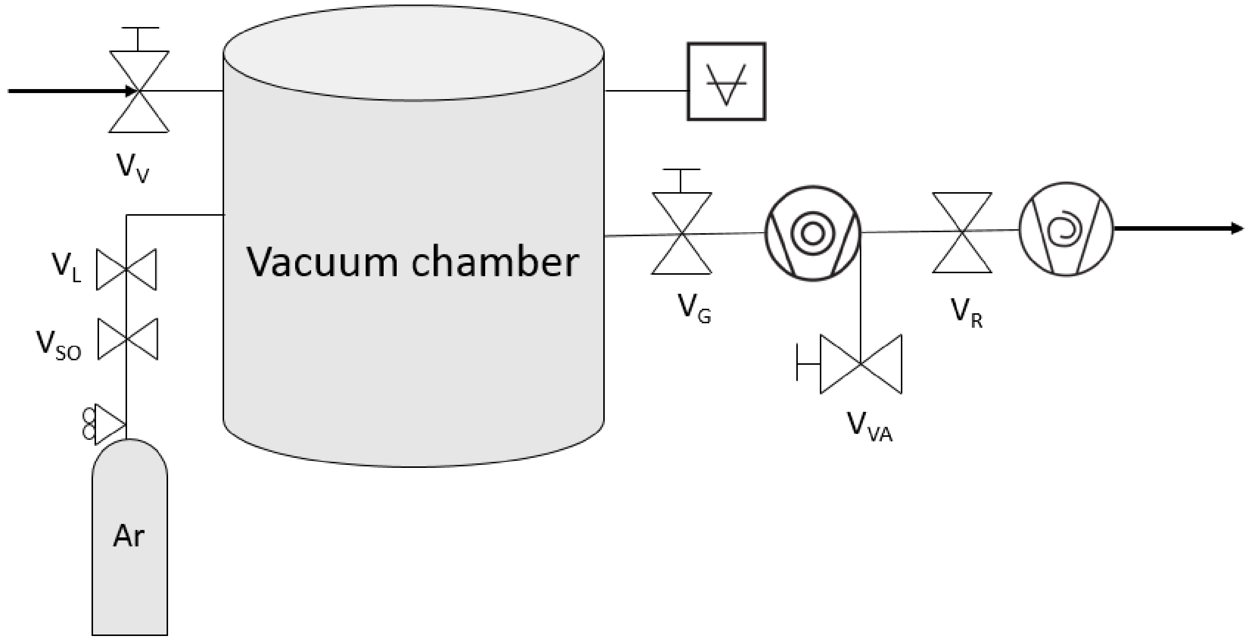
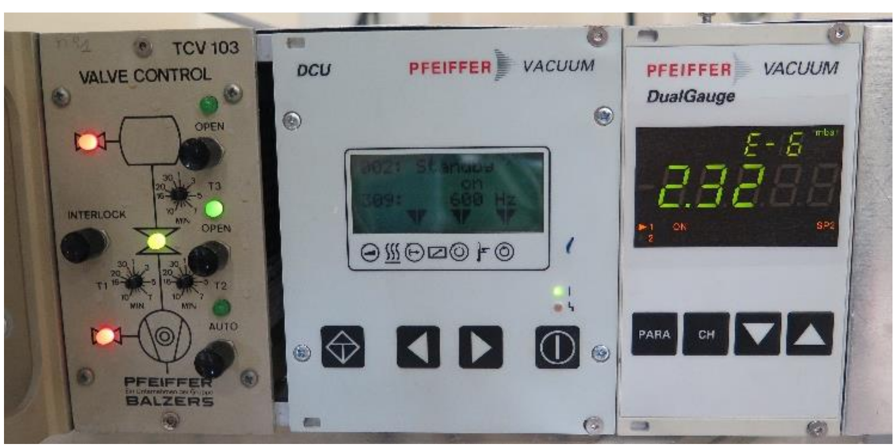


Figure 3.1: Diagram of vacuum system.

In the diagram mentioned before, valves, pump, vacuum chamber and argon cylinder are shown. The valves are represented with the letter V and the sub-indexes dictate the type of valve (V: venting, G: gate, L: leak, SO: shut-off, R: rough, VA: venting automatic). This configuration ensures the proper functioning of the pumps. Each instrument will be described later in this chapter.

In Figure 3.2 (a) a picture of the complete system is shown and in Figure 3.2 (b) the control panel can be observed. There are three parts in the panel: the valve control, the pump control and the pressure gauge measure. The valve control allows to open or close venting and gate valves. The pump control allows to regulate the pumping velocity of the turbo molecular pump: stand by for normal pumping (600 Hz) and high speed (1000 Hz). The gauge measure shows the measure of pressure.

(a)



(b)

Figure 3.2: (a) Vacuum system. (b) Control panel.

3.1.1 Vacuum chamber

The chamber is made of stainless steel and has a cylindrical form with dimensions of 53 cm diameter and 55 cm tall. This chamber has a view port (CF 100) available in order to make sure that the position of the sample holder is aligned with the magnetron and the appearance of the plasma during deposition. The picture in Figure 3.3 shows the view from the port and the positioning between the magnetron and the sample holder.

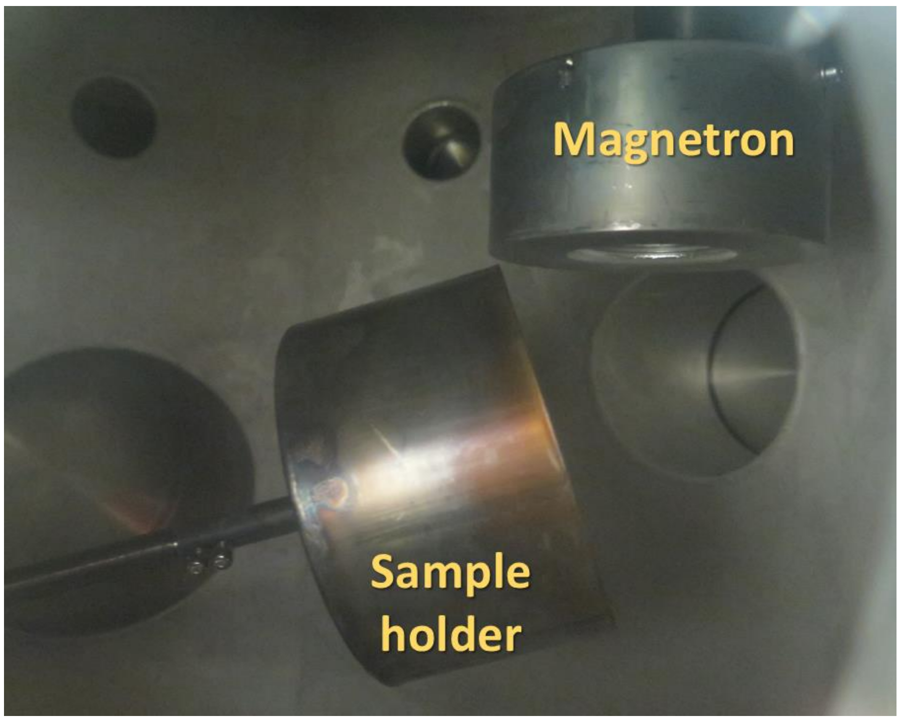


Figure 3.3: Magnetron and sample holder position inside the chamber.

The magnetron has an inner part that includes a cooling system by water with its correspondent silver target. The magnetron is cylindrical, such as the magnetron type showed in CHAPTER 2. It is important that the magnetron is positioned near the sample holder but without contact.

The chamber is cleaned before each deposition process. It is cleaned with a vacuum cleaner and the parts inserted into the chamber are cleaned with alpha wipes and ethanol.

The connection between the chamber and the pumping system is made from the bottom of the chamber beginning with the gate valve. The chamber can be open from the upper part and to open it there is a crane available. This disposition allows a comfortable way of working to prepare and position the sample holder, as well as to clean the chamber easily.

3.1.2 Pumps

This system consists in two pumps in order to produce vacuum in the chamber. First, the pumping system includes a primary Varian Scroll pump that can be seen in the Figure 3.4. This pump, model Triscroll 300, is oil free and can reach pressure of 10^{-2} mbar.

Figure 3.4: Varian Scroll pump.

Inside a Scroll pump, three intercrossed spirals move in order to expulse air of the system. Usually, one of these spirals is fixed and the others orbit without rotating. Air enters into the spirals and when particles reach the center, they are expulsed.

The second pump, is a Pfeiffer turbomolecular pump of 230 liters per second (Figure 3.5). This configuration can reach a vacuum pressure of approximately 10^{-7}mbar. Turbo molecular pump functioning is based on rotation movements of several opposite blades. Blades rotate with a high speed motor that can reach (in this case) 1000 Hz. The blades rotation transfers mechanical energy to gas molecules, with this energy, molecules moved through the pump until they are extracted. Due to this fast motion, two cooling fans are located around the pump.

Figure 3.5: Turbomolecular pump.

3.1.3 Gauges and valves

This vacuum system includes several gauges to control the process and insertion of gases. The low vacuum gauge (until 10^{-3}mbar) is a Pirani valve made by Pfeiffer and the high vacuum Bayard-Alpert gauge that can reach 10^{-6}mbar, are both used for pressure measurements.

On the other hand, there is a manual valve to control the entrance of the working gas Argon which is controlled by a leak valve. For the venting, there are two valves available, a manual one and an electro-pneumatic one for the insertion of nitrogen gas.

3.1.4 Power supply

The system needs a power supply to give energy necessary to produce plasma, and in this way, to produce the sputtering process. In this work, a MDX Magnetron Drive power supply was used (Figure 3.6).

Figure 3.6: Power supply.

The power supply is connected directly to the magnetron to produce a difference of potential. In this work, the current was 0,15A and 0,2A. These current values were taken from previous work, made in the framework of a previous edition of the Master in Surface Treatments.

3.1.5 Motor

In order to reproduce a method for sputter a good coating for the seeds, it is necessary to have a continuous movement during the deposition. The motor used during this work is shown in Figure 3.7. This motor has a rotational axis that enters the chamber and holds the sample holder.

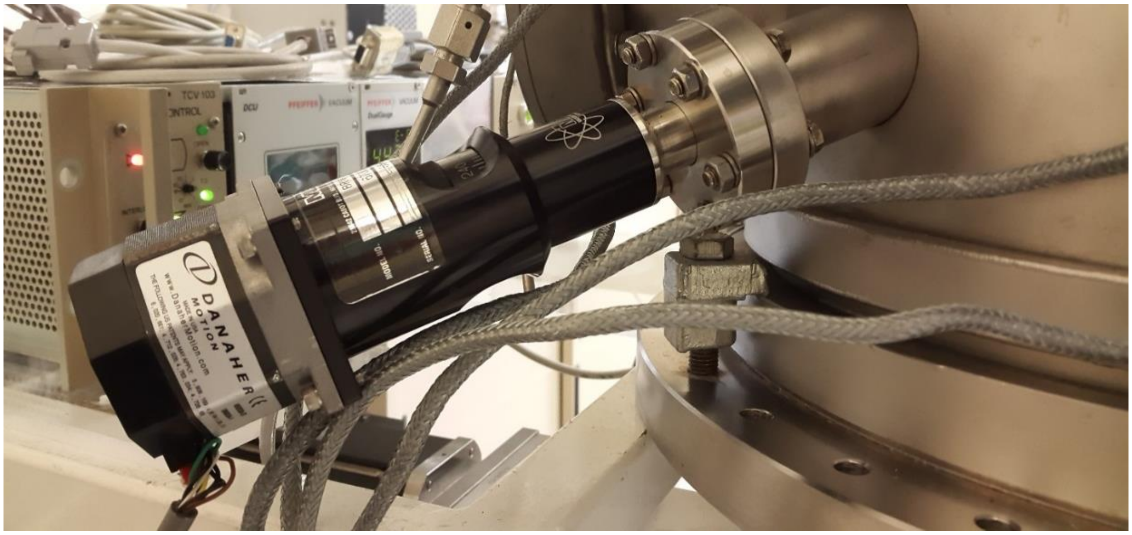


Figure 3.7: Motor for the sample holder rotation.

This motor is controlled by a computer software in which the user can choose the velocity of rotation and if the rotation is continuous or by steps. During all the work, the velocity chosen for the deposition was 5 turns per minute. A screenshot of this software can be seen in Figure 3.8.

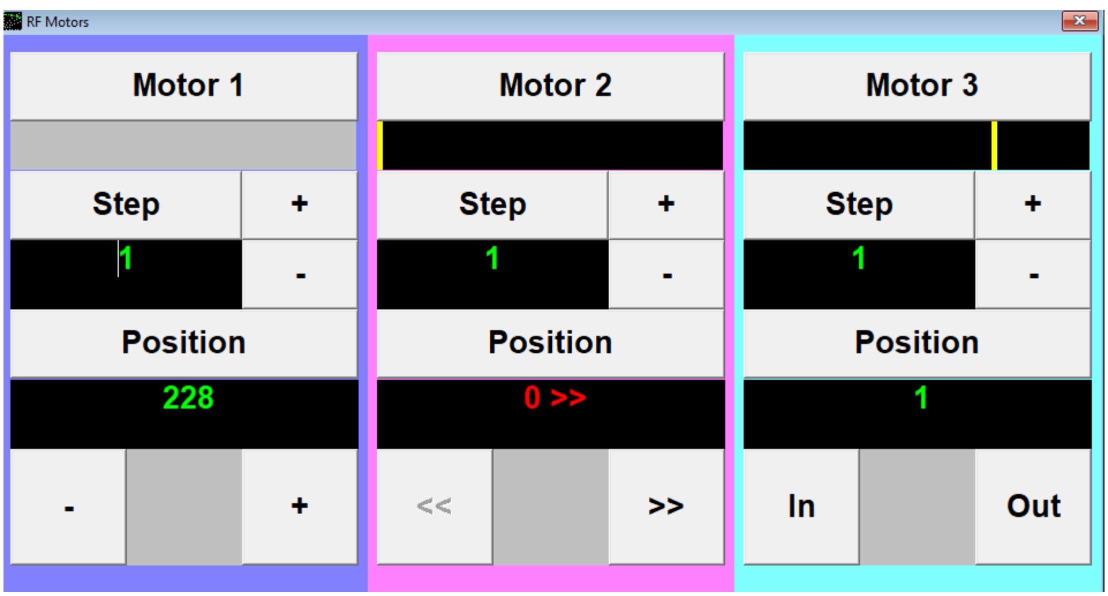


Figure 3.8: Motor control software.

CHAPTER 4

COATING PROCESS

Several combinations in the seeds preparation were made before and/or after the deposition of the seeds. Including the wet (chemical) and dry (physical) treatments named in the previous chapter. The wet treatment was made in order to reduce the size of the seeds (for the seeds aspect could be similar to silver cardamom seeds sell in market) and the dry treatment for the improvement of seeds surface.

4.1.1 Preparation of seeds

Preparation of seeds was made in several steps depending on the sample. If the sample needed a reduction of size, the first step was applying the chemical treatment for the seeds. The second step is the physical treatment. This treatment was also used by introducing sugar in the recipient along with the seeds to in order to accelerate the process when the seeds alone were not making sufficient friction to make the seeds surface homogeneous.

Figure 4.1: Prepared seeds to be put in the tumbler machine before deposition.

After the chemical and physical treatments of the surface of seeds, next step was: deposition. The physical treatment was repeated in some samples also after the deposition as a post sputtering treatment.

4.1.2 Depositions

Depositions were made in the vacuum chamber with all the instrumentation showed previously, in which an Argon plasma with pressure $5x10^{-3}$ mbar is produced by a current of 0,2 or 0,15 A (depending on the sample). In total, twenty (20) depositions were made, each of them with different preparation or deposition parameters. Samples were identified as CD from 01 to 20.

Two sample holders were used during this investigation. In the firsts depositions we used a sample holder as can be seen on the left in Figure 4.2. The first sample holder used (left) measures 20 cm diameter and 8 cm depth; second sample holder (right) measures 11,5 cm diameter and 6 cm depth.

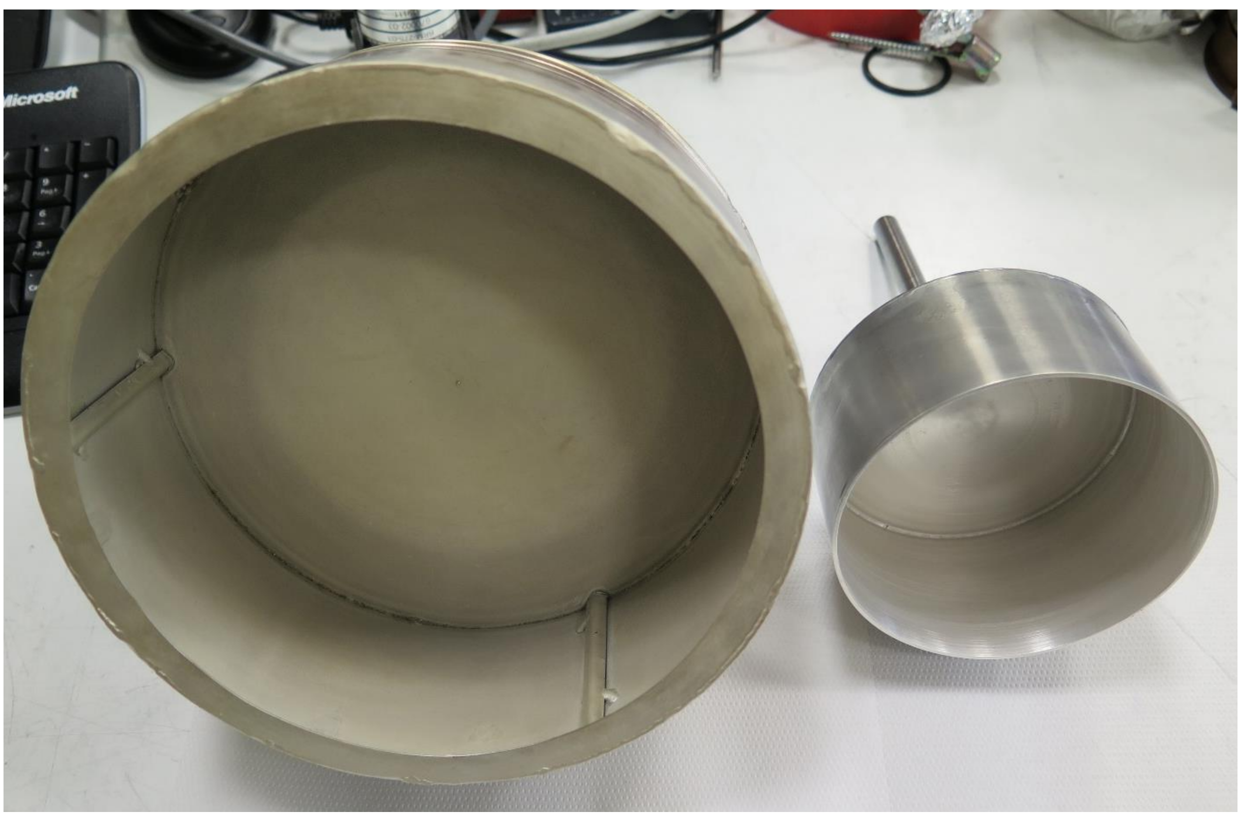


Figure 4.2: Sample holders used.

The first depositions were made with a big sample holder and deposition parameters that were investigated in previous works. The work pressure, was fixed at $5x10^{-3}$ mbar, which is the pressure after introducing the Argon gas to the chamber (Zordan, 2015). The sample holder had a rotation controlled by a motor of 5 rounds per minute, in this way the seeds can be deposited homogeneously in their entire surface.

A summary of the depositions and treatments of each sample can be observed in the Appendix. Samples CD-01, CD-02 and CD-03 were coated for 15, 30 and 45 minutes respectively. These depositions were made in steps of 15 minutes each. These three samples presented opaque appearances and dark colors. In Figure 4.3 the seeds after 3 deposition of 15 minutes each are shown.

Figure 4.3: CD-03 sample.

Next deposition (CD-04), was made for 15 minutes but rotation was made in intervals of 30 seconds and pauses of 30 seconds. Even though the seeds still presented an opaque appearance but a less dark color. For the next sample, CD-05, the distance between the sample holder and the magnetron was reduced and the same time of deposition was tried in order to study the changes produced. In this deposition, an attachment of the seeds was observed. In Figure 4.4 both CD-04 sample (a) and CD-05 sample in (b) are shown.

(a) (b)

Figure 4.4: (a) CD-04 sample, (b) CD-05 sample.

CD-06 was the next deposited sample. In 4 steps of 15 minutes each with pauses of five minutes between them to avoid the attachment of seeds (Figure 4.5). Also, for this sample more quantity of seeds were put into the sample holder. The appearance of the seeds continued being opaque with a dark color.

Figure 4.5: CD-06 sample.

With the six previous samples, it was noticed that the surface of the seeds needs to be regular without any defect. This means that it was necessary to perform some improvements in the surface of the seeds.

For CD-07 sample, a physical process was made before deposition. The seeds were put into the tumbler machine for 24 hours. In Figure 4.6 it is possible to see how the surface of the seeds changed after the tumbling. The surface is flatter so the seeds had a brilliant appearance before deposition.

(a) (b)

Figure 4.6: CD-07 (a) Before tumbling (b) After tumbling.

Deposition for these seeds was made for 15 minutes; the appearance was still dark and opaque but with a visible improvement. For this reason, seeds were deposited for another 15 minutes to observe if the thickness increasing changed the appearance. These 30 minutes coating seeds were called CD-08 (Figure 4.7).

Figure 4.7: CD-08 sample.

The physical process in the tumbler showed an improvement in the surface of the seeds. For this reason a longer process was made. For CD-09 sample, the tumbling was made for 3 days. After 15 minutes deposition the appearance of the seeds improved and became less dark (Figure 4.8).

Figure 4.8: CD-09 sample with 3 days physical treatment before deposition.

After this improvement, the sample holder was changed by a smaller one so the seeds could be closer to the target. This sample holder is completely flat in the inner part, this way we can ensure that the seeds moves continuously. Until CD-09, the vacuum order of magnitude was around 10^{-5} mbar; for the next sample, the vacuum achieved was 10^{-6} mbar. An extra 15 minutes coating was made and the appearance was silver-like as can be seen in Figure 4.9.

Figure 4.9: CD-10 samples with silver appearance.

With this sample, we could notice a considerable improvement when the base pressure or the pressure before deposition is lower. On the other hand, the closeness between the seeds and the magnetron played a decisive role.

It is necessary that the process for the silver coating in the Cardamom seeds can be reproducible and optimized. For these reasons, different samples were probed changing parameters as: current, time, treatments, base pressure, etc. The next sample, called CD-11, were tumbled for 40 hours before deposition and the current was reduced to 0,15 A in order to avoid the attachment between the seeds. The time for this deposition was 15 minutes, but made in three steps of 5 minutes each and pauses of 5 minutes between the steps. However, the seeds were attached to one another.

Figure 4.10: CD-11 sample.

During this optimization process, the time of deposition and the tumbling was changed for the next sample. For CD-12 deposition was made for 15 minutes in steps of 1 minute and pauses of 30 seconds. This configuration was chosen in order to avoid the heating and attachment between the seeds. The tumbling lasted three days in order to improve the surface of seeds and so the silver coating improved, as shown in Figure 4.11.

Figure 4.11: Comparison between last two depositions. Left side CD-11, right side CD-12.

For both samples, CD-11 and CD-12, a post sputtering treatment was applied. The seeds were put in the tumbler machine for 24 hours in order to observe changes. This procedure produced a shine appearance to the seeds. For example, in Figure 4.12 it is possible to observe this change where even a mirror appearance is present.

Figure 4.12: Comparison between CD-12 seeds before and after post sputtering treatment.

Although the silver coating has a silvered appearance, it is necessary to reduce the size of the seeds. As the seeds have a sugar and water cover, a chemical treatment was made to CD-13 samples to dissolve it. In this way, the size of the seeds is reduced to a desired size. The chemical treatment was made with a solution of water and alcohol at 50% for three minutes. Later, tumbling was made for two days and then coated as previous samples. Deposition was made in three steps of five minutes each with pauses of three minutes between each process.

These seeds had an opaque appearance as can be seen in Figure 4.13 (a). The surface of the seeds is not flat and it is possible to observe some "bumps". For this reason, the seeds were tumbled after deposition for 24 hours, and the appearance changed but until the coating had practically disappeared (see Figure 4.13 (b)). This can be due to non-adhesion of the coating to seeds.

(a) (b)

Figure 4.13: CD-13. (a) After deposition. (b) After tumbling post sputtering.

In order to understand the change in the seeds with dissolution, two samples called CD-14A and CD-14B were dissolved for five and seven minutes respectively with the chemical treatment named before. These seeds were tumbled for five and seven days respectively. Seeds after dissolution and tumbling can be seen in Figure 4.14.

(a) (b)

Figure 4.14: CD-14 A (5 minutes dissolution) and B (seven minutes dissolution) before coating.

The difference in tumbling time is due to the roughness of the seeds surface. The longer the time that the seeds are dissolved, the less flat or less homogeneous the surface is. The deposition was made in three steps of five minutes each, with three minutes pauses between each step.

(a) (b)

Figure 4.15: CD-14 A and B after deposition process.

Both of these samples (CD-14 A and B) had an opaque appearance because the surface of the seeds is not flat. For this reason, CD-15 sample was dissolved for seven minutes and tumbled with sugar for 24 hours before the deposition process. In Figure 4.16 it is possible to see some improvements on of the appearance of the seeds by changing only the tumbler process and using the same deposition parameters and time.

Figure 4.16: CD-15 sample.

Following the improvement procedure, a longer time of tumbling process was tried. Next sample was also dissolved for seven minutes but the tumbler process with sugar lasted three days. In Figure 4.17 the silver appearance of the seeds when the surface is improved can be seen.

Figure 4.17: CD-16 sample.

For the next sample, dissolution time was increased up to ten minutes to obtain smaller seeds. The main problem with this dissolution time is that the sugar covering the seeds in some cases is completely dissolved. The tumbling process used was the same as in previous sample (3 days). Depositions time was 20 minutes total made in four steps of five minutes each. Between each steps there were pauses of three minutes in order to cool down the seeds and prevent them from attaching together.

In Figure 4.18 is shown the seeds after deposition with a dark appearance. But it is important to consider the base pressure of this deposition. For previous depositions the base pressure was in the order of 10^{-6} mbar, for CD-17 was 10^{-5} mbar.

Figure 4.18: CD-17 sample.

For the next sample, CD-18, dissolution time was changed to seven minutes. The seeds were tumbled for three days before deposition. The process was made the same way as before, four steps of five minutes each. In this sample, it is possible to observe an opaque appearance but with less dark color (see Figure 4.19).

Figure 4.19: CD-18 sample.

It is convenient to compare CD-18 sample with CD-16 sample. Both samples were dissolved for seven minutes and tumbled for three days before deposition. The only parameter that changed was the deposition time from 15 minutes to 20 minutes. Also, the base pressure in CD-16 was lower than in CD-18, $7{,}44\text{x}10^{-6}$ mbar and $9{,}49\text{x}10^{-6}$ mbar respectively. This is the main reason for another measurement with the same deposition parameters but with lower base pressure.

CD-19 was done with a base pressure of $5{,}7\text{x}10^{-6}$ mbar. This seed had a silver and shine appearance, in this way it is demonstrated that the base pressure represents a fundamental parameter for the appearance of the seeds.

Figure 4.20: CD-19 sample.

The last sample was called CD-20. In this sample dissolution time was 8,5 minutes to obtain smaller seeds. These seeds were tumbled with sugar for three days and sputtered for 15 minutes in three steps of five minutes each. Even though these seeds are smaller, in some parts the sugar covering was completely dissolved, in comparison with CD-19 that the covering is complete in all seeds.

Figure 4.21: CD-20 sample.

As an illustration, a comparison between commercial silver cardamom seeds and silver Cardamom seeds coated by magnetron sputtering technique is made in Figure 4.22

Figure 4.22: Comparison between commercial silver Cardamom (left) and silver Cardamom produced in the aim of this work (right).

4.2 SEM analysis

In the framework of this investigation, a seed was observed with the SEM. The first thing to consider is the malleability of silver. For this reason, seed was frozen in liquid nitrogen and then cut in half to observe the thickness of the coating with the SEM.

When the seeds are introduced in liquid nitrogen, the sugar coating starts to be dissolved, so part or the coating is eliminated. For this specific reason, we can obtain an idea of thickness, but not an accurate measure. In Figure 4.23, it is possible to observe different parts that are contained in the seeds. The inner part is the seed itself, then is covered by a sugar envelop and finally the silver coating.

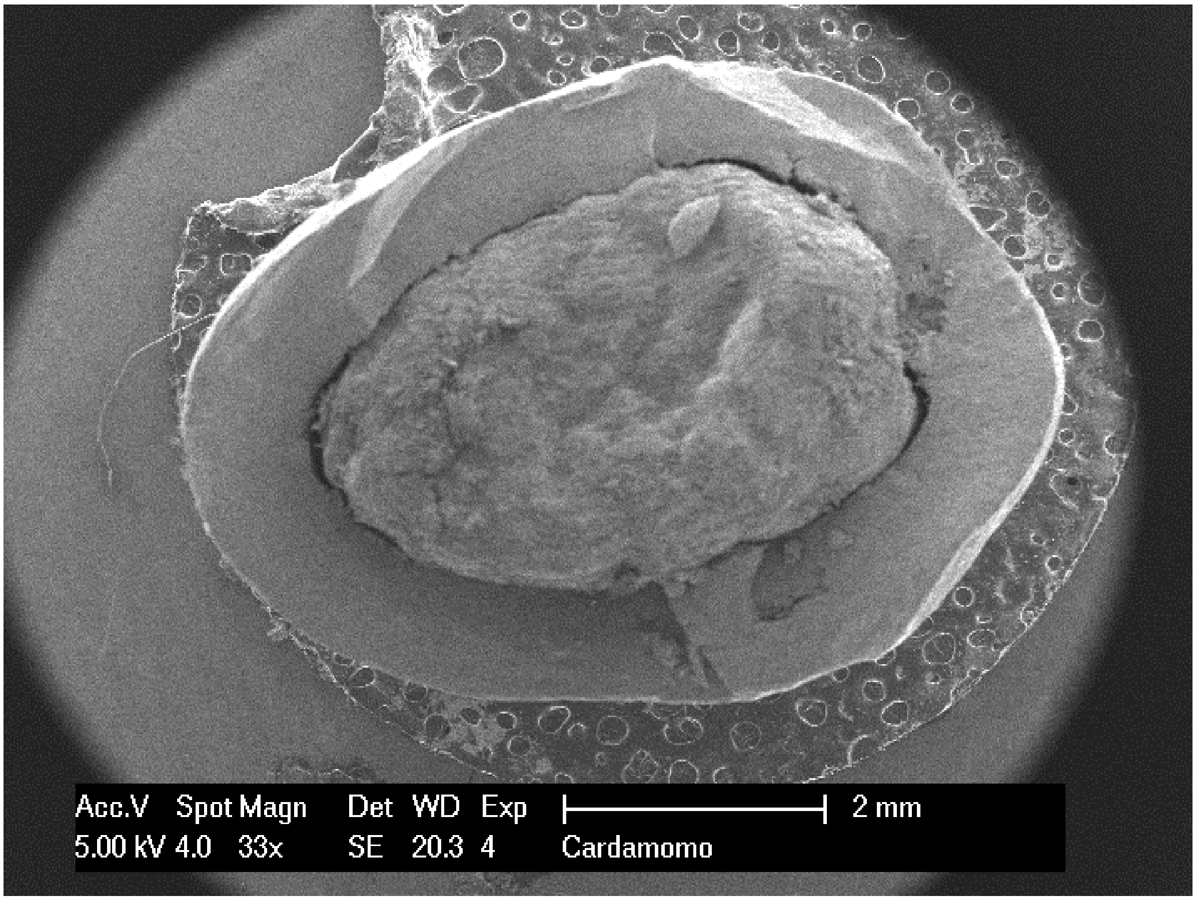
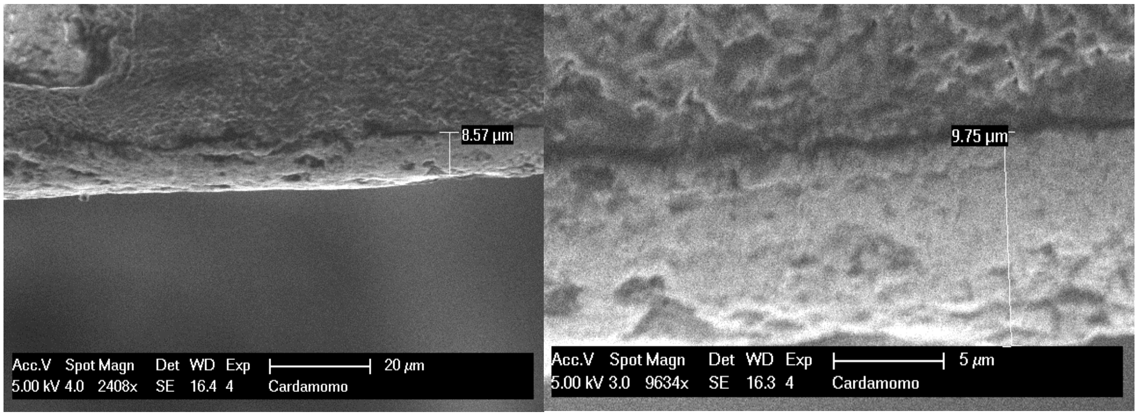


Figure 4.23: Cardamom seeds observed with SEM.

The seed itself (if it is considered as a sphere) measures approximately 3,5 millimeters of diameter. The sugar envelop is about 1 mm and the silver coating (as can be seen in Figure 4.24) is about 10 microns. In (a) Figure 4.24 a measure of 8,57 μm was done while in (b) a measure of 9,75 μm. These two measurements were made using different zooms and scales (2408X and 9634X respectively).



(a) (b)

Figure 4.24 : Measurements of silver coating thickness made with SEM.

During observations with the SEM, it was noticed that the coating is not uniform (due to the dissolution in liquid nitrogen mentioned before). Also, it was noticed that the voltage applied during the analysis cannot exceed 10 kV. In Figure 4.25, it can be observed in red a bubble kind of figure that appeared during the analysis when the voltage was increased due to the heating.

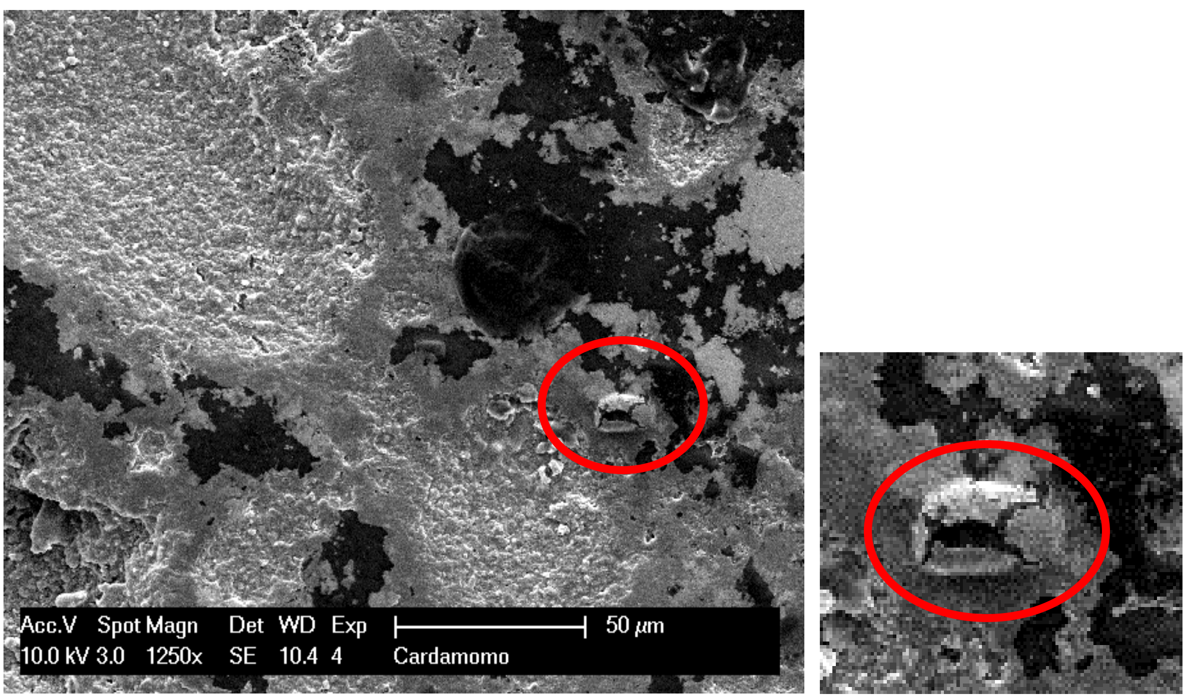
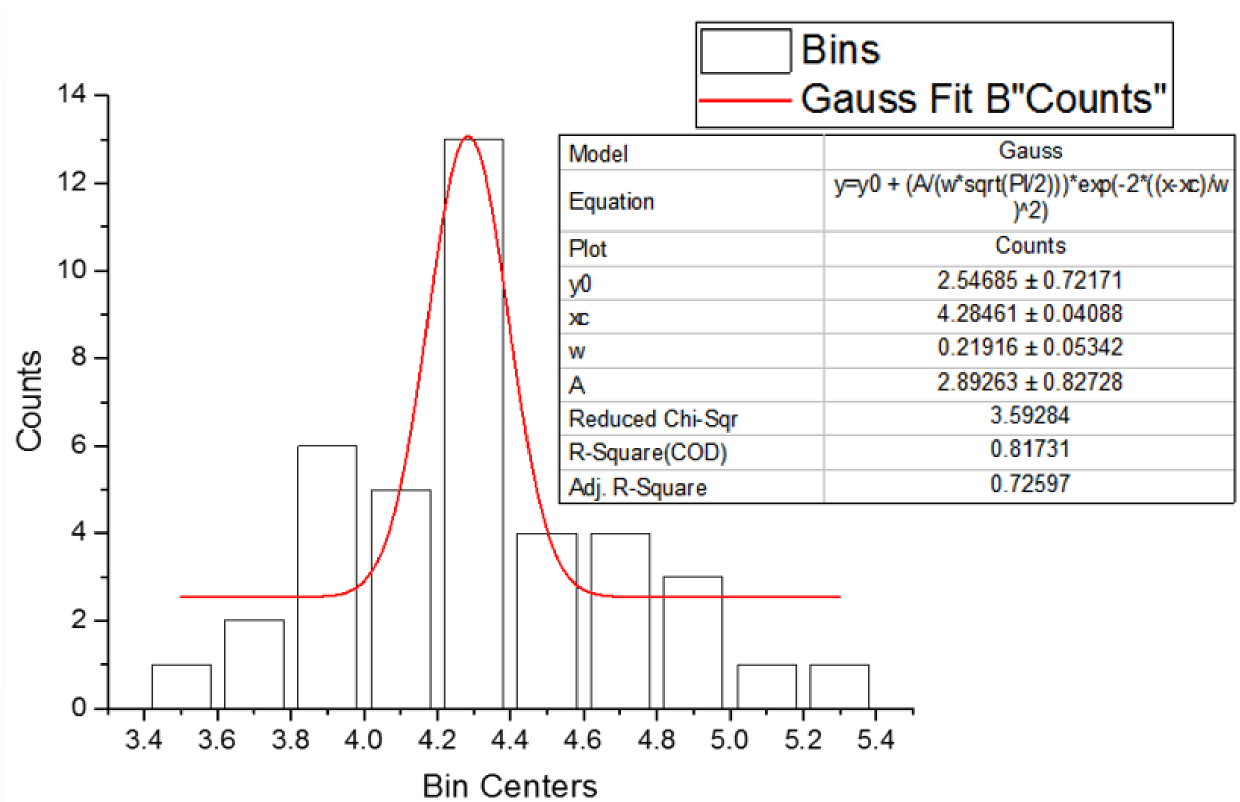


Figure 4.25: Picture with SEM with detail in red.

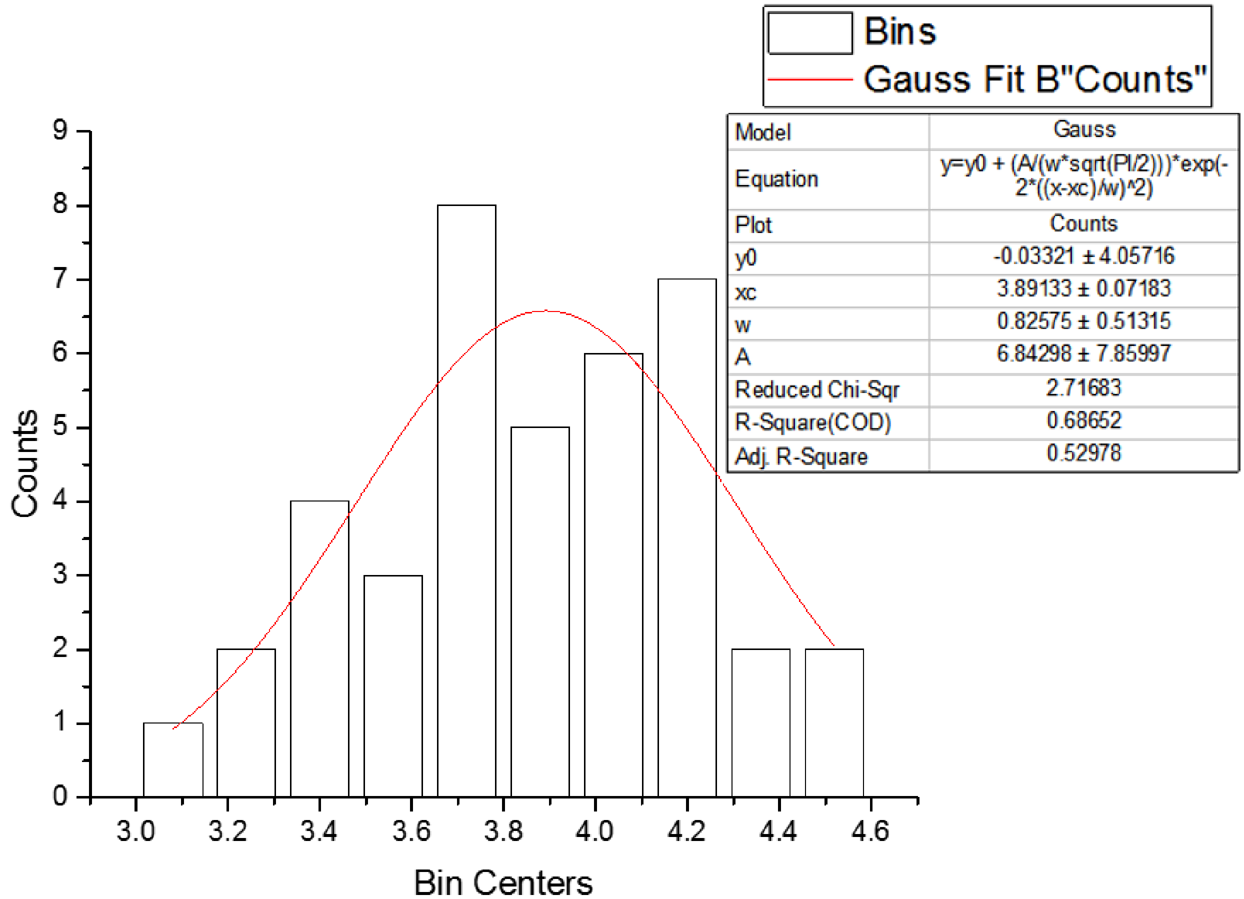
4.3 Dissolution thickness measurement

In order to measure the thickness of the layer removed from the seeds by the dissolution, the diameter before and after the dissolution were measured on two samples of 40 seeds each. The samples were dissolved seven and ten minutes respectively. Histograms of frequency of the diameter of the seeds were made to both samples before and after dissolution.



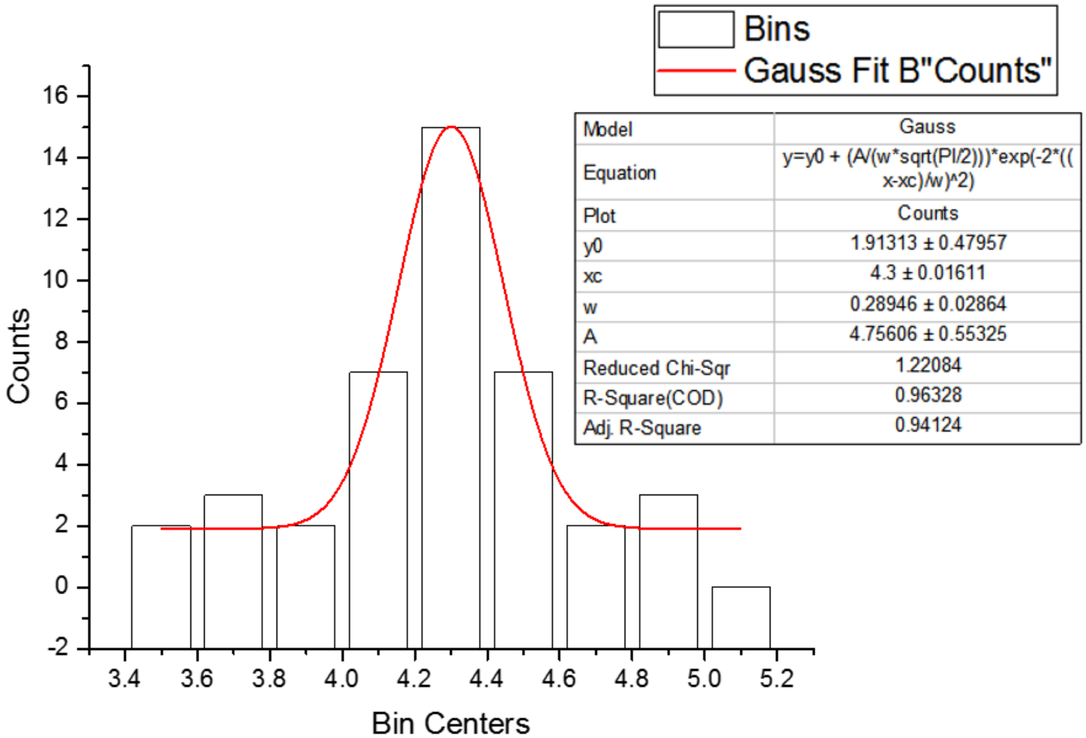
Graph 4.1: Histogram of frequency of the diameter of seeds (mm) before 7 minutes dissolution.

In the graph showed before (Graph 4.1), a histogram of the diameter of the seeds was made, considering the seeds as spheres. This diameters were measured with a caliper before the 7 minutes dissolution. Next graph (Graph 4.2) represents the histogram of the thickness of seeds after dissolution with its correspondent fitted Gaussian. The center of the fitted Gaussian was consider for the calculation of the removed layer.

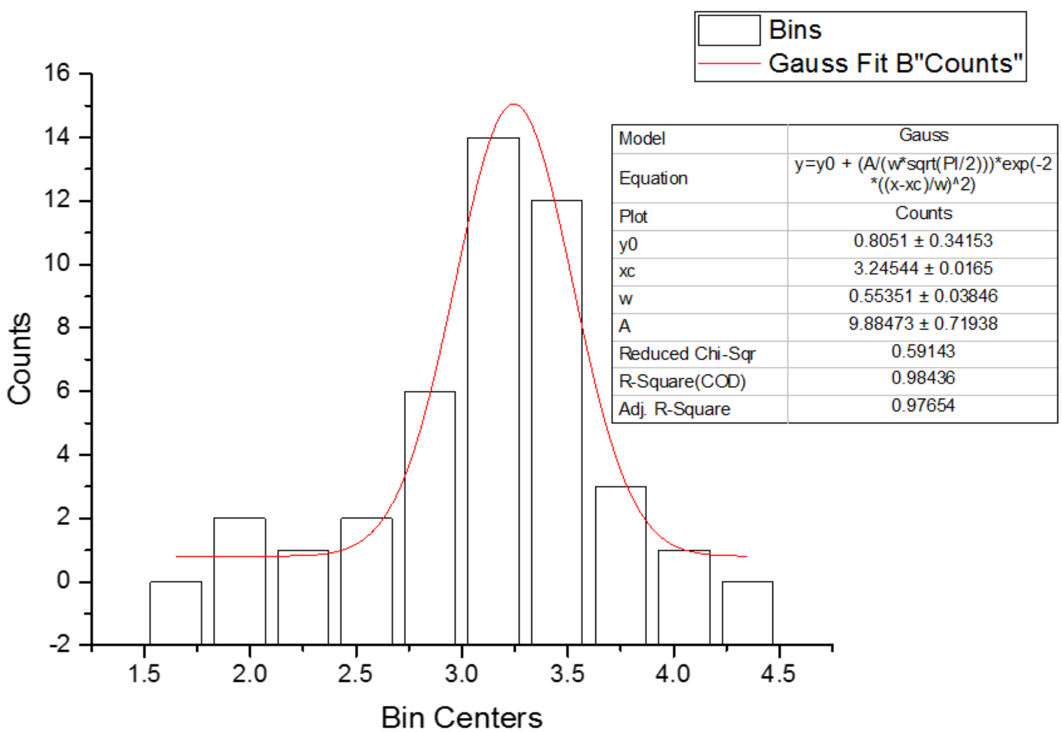


Graph 4.2: Histogram of frequency of the diameter of the seeds (mm) after 7 minutes dissolution.

For the sample dissolved for 10 minutes, the same procedure was applied. In Graph 4.3 it is shown the histogram of the diameters of the seeds measured before dissolution of the seeds in water and alcohol described before. Histogram of the measurements of the diameter of the seeds after the dissolution are shown in Graph 4.4.



Graph 4.3: Histogram of frequency of the diameter of seeds (mm) before 10 minutes dissolution.



Graph 4.4: Histogram of frequency of the diameter of the seeds (mm) after 10 minutes dissolution.

Taking into consideration the centroids of the fitted Gaussians before and after dissolution of 7 and 10 minutes, the removed layer calculated was 0.21 mm and 0.53 mm respectively. These results can be translated in a dissolution rate of 0.03 mm/s for the 7 minutes dissolution sample and 0.05mm/s for the ten minutes dissolution sample. From these results it is not possible to assume that dissolution is a linear reaction that can be due to the manual agitation of the solution during the dissolving process. One way to improve this incongruity is to dissolve the seeds in an agitator.

4.4 Profilometer

In order to measure the thickness of the silver coating in the seeds, a quartz sample was sputtered for ten minutes with the same parameters of seeds deposition (same work pressure and 1,5 A current). The quartz sample is 10mm x 10mm and is shown in Figure 4.26. The sample was introduced into the same sample holder as the seeds rotating at 5 turns per minute (same velocity as CD samples). The difference of thickness between an unsputtered area and a sputtered area was measured with the profilometer available in the laboratory and described in the previous chapter.

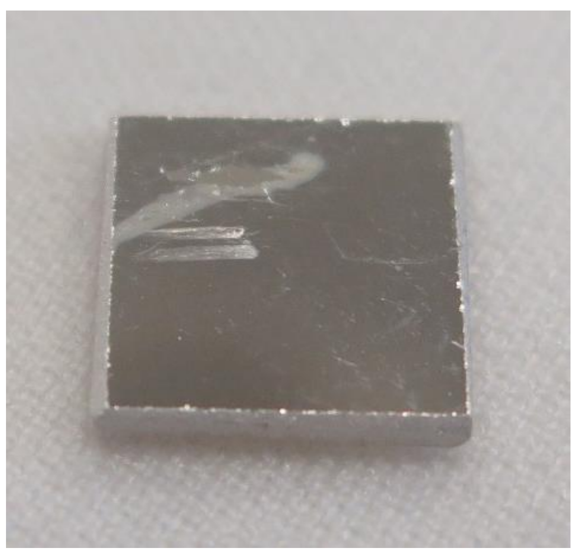


Figure 4.26: Quartz sample.

The measurements were made beginning in three different points. These measures are obtained from a graph provided by the profilometer software. In Figure 4.27, it is possible to observe one of the measures made.

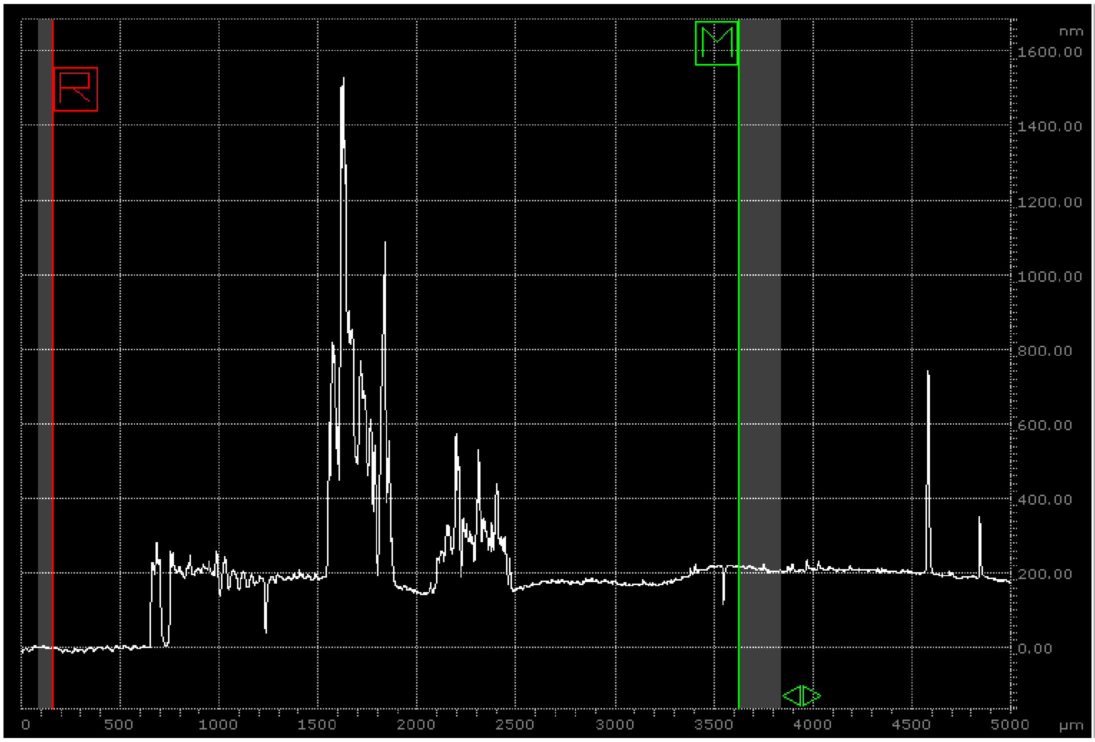


Figure 4.27: Profilometer thickness measure for a ten minutes sample deposited.

It is important to consider that the sample was sputtered for ten minutes, so it is not directly a measurement of the thickness of the silver coating made to the seeds.

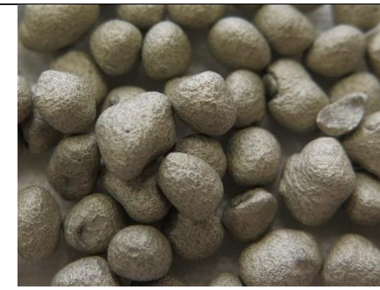
SCHEME OF THE EXPERIMENTAL RESULTS

Sample	Base pressure (mbar)	Deposition time (min)	Appearance	Considerations	Picture
CD-01	N/M	15	Opaque		
CD-02	N/M	15 + 15	Opaque		
CD-03	N/M	15 + 15 + 15	Opaque		

CD-04	N/M	15	Opaque	Rotation stop every 30 sec for 30 sec	
CD-05	N/M	15	Opaque	Magnetron and sample holder closer	
CD-06	N/M	15 + 15 + 15 + 15	Opaque	5 min between each deposition	

CD-07	3.49 x 10-5	15	Opaque	1 day tumbling (half filled)	
CD-08	2.62 x 10-5	15 + 15	Opaque		
CD-09	3.92 x 10-5	15	Silver	3 days tumbling before deposition	
CD-10	7.21 x 10^{-6}	15 + 15	Silver	Improved vacuum, smaller sample holder.	

CD-11	7.80 x 10^{-6}	5 + 5 + 5	Silver	40 hours tumbling before deposition. 5 minutes pauses between depositions.	
CD-12	8.33 x 10^{-6}	15 processes of 1 minute each	Silver	3 days tumbling. Pauses of 30 seconds between each step. 1 day tumbling after	
CD-13	5.61 x 10^{-6}	5 + 5 + 5	Opaque	2 days tumbling before coating. Pauses of 3 min between each step.	
CD-14 A	9.07 x 10^{-6}	5 + 5 + 5	Opaque	Pauses of 3 min between each step. 5 days tumbling before coating and 1 day after. 5 minutes dissolved.	

CD-14 B	7.67 x 10^{-6}	5 + 5 + 5	White	Pauses of 3 min between each step. 7 days tumbling before coating and 1 day after. 7 minutes dissolved.	
CD-15	5.03 x 10^{-6}	5 + 5 + 5	Silver	Tumbled with sugar for 1 day before deposition. 7 minutes dissolved.	
CD-16	7.44 x 10^{-6}	5 + 5 + 5	Silver	Tumbled with sugar for 3 days. 7 minutes dissolved.	
CD-17	1.04 x 10^{-5}	5 + 5 + 5 + 5	Opaque	Tumbled with sugar for 3 days. 10 minutes dissolved.	

CD-18	9.49×10^{-6}	5 + 5 + 5 + 5	Opaque	Tumbled with sugar for 3 days. 7 minutes dissolved.	
CD-19	5.70×10^{-6}	5 + 5 + 5	Silver	Tumbled with sugar for 3 days. 7 minutes dissolved.	
CD-20	5.08×10^{-6}	5 + 5 + 5	Silver	Tumbled with sugar for 3 days. 8,5 minutes dissolved.	

N/M: not measured.

CHAPTER 5

CONCLUSIONS

Taking into consideration the importance of the Indian culture for the rest of the world, the aim purpose of this work was to produce coated edible seeds with a good size and appearance for the Indian market. Silver and cardamom seeds are usually consumed in India for health reasons, but the manufacturing of silver sheets or Varak is by hand and can produce Argyria disease for the workers. Cardamom seeds with silver coating are usually consumed as a snack in India, especially for aid breathing. In order to change the manufacturing process of such a common Indian food, cardamom seeds were treated to enhanced the handcraft process and find a safer way to produce the final product. For this reason, in this work Cardamom seeds were coated with the magnetron sputtering deposition technique in a vacuum chamber where an Argon plasma is produced.

Cardamom seeds were deposited in a rotary sample holder for homogeneity of the coating. Surface treatments were indispensable to obtain a good coating. Chemical treatment was used to reduce the size of the seeds in order to obtain coated seeds similar to commercial silver Cardamom seeds. Cardamom seeds for this work, were covered with a buffer layer of sugar and water with the purpose of avoid degassing that tarnished seeds. The seeds were introduced for different times in a solution of water and alcohol at 50% to dissolve the sugar envelop. Physical treatment was used to improve the surface of the seeds, i.e. to make them smoother. It consists of placing the seeds in a tumbler machine where they can touch each other and the friction eliminates irregularities of their surfaces. To improve this friction, the seeds were tumbled in a plastic recipient with sugar.

Twenty (20) samples were treated during this work with different times and preparations of seeds before and after sputtering. The sputtering parameters were 0,15 A of current and argon pressure of $5x10^{-3}$ mbar. The base pressure is a fundamental parameter in the appearance of the seeds after deposition. The lower the base pressure, the better the coating if the other parameters are the same.

With surface treatments as chemical dissolution and physical tumbling, it was possible to obtain small deposited seeds with a brilliant and silver appearance. Taking into consideration the results of the studied samples during this work, the best procedure obtained was: dissolution of the sugar covering of the seeds during 7 or 8,5 minutes in a solution of water and alcohol at 50%; formerly, a tumbling process with sugar for 3 days and then sputtering process of 15 minutes in 3 steps of 5 minutes each with correspondent pauses between steps. The pauses are made in order to avoid the seed to get attached to each other due to the heating during the process. In the two cases with better results, the base pressure was under $8x10^{-6}$ mbar.

Thickness of silver coating on Cardamom seeds measured 9 microns and was made with SEM. A seed was immersed in liquid nitrogen in order to make a single and precise cut, but liquid nitrogen dissolved part of the silver coating. For this reason, it is possible that this measurement is not reliable. On the other hand, a measurement with profilometer was made to a quartz sample of 300nm, which cannot be compared because it is not a direct coating thickness measurement. Both measures are very different and it is not possible to know from these measurements an accurate thickness of the deposited coating.

Using the procedure described above, it was possible to obtain smaller, and shiner seeds, improving their appearance in a considerable manner. This procedure promotes a new and safer method to replace the actual and dangerous handcrafting method of coating with silver the cardamom seeds.

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