Ultra thin film deposition of nickel, cobalt and nickel-cobalt and evaluation using scanning acoustic microscopy

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Ultra Thin Film Deposition of Nickel, Cobalt and Nickel-Cobalt and 
Evaluation Using Scanning Acoustic Microscopy

by

Annamarie Balutiu

A Thesis
Submitted to the Faculty of Graduate Studies through Chemistry and Biochemistry in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor Windsor, Ontario, Canada

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Abstract

In the last few years, ultra-thin films have been widely adopted in medical and industrial applications; especially the dielectric implants coated with porous ultra thin films used in medical field. In the present investigation, a combination of two techniques was used: a classic one for the deposition of ultra thin films (i.e., electroless deposition) and a complementary non-destructive technique (i.e., scanning acoustic microscopy) for quality evaluation of nickel cobalt ultra thin films grown on a dielectric substrate. The developed method is useful for further improvement of designing and manufacturing of the films.

In order to evaluate interface conditions with maximum sensitivity, high frequency (i.e., 600 MHz and 1 GHz) was employed. A highly focused ultrasonic beam emitted from a high numerical aperture enhanced contrast in the image. Therefore, the image showed minute details (i.e., porosity, micro-cracks, delaminations, detect poor adhesion at the interface), that other conventional microscopes have difficulty visualizing.
Dedication

I would like to dedicate this thesis to my mother and my fiancée Goran who have always supported and encouraged me to pursue my dreams and goals.
Acknowledgements

A special thanks to my supervisor Dr. Elena Maeva for her help and for always being a source of encouragement, for introducing me to the interesting field of scanning acoustic microscopy, and not to be forgotten for accepting me in her research group.

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<tbody>
<tr>
<td>AARC</td>
<td>Acoustic antireflection coating</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>BH</td>
<td>Borohydride</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DMAB</td>
<td>Dimethylamineborane</td>
</tr>
<tr>
<td>DMB</td>
<td>Double balanced mixer</td>
</tr>
<tr>
<td>ELD</td>
<td>Electroless deposition</td>
</tr>
<tr>
<td>EN</td>
<td>Electroless Ni deposition</td>
</tr>
<tr>
<td>II</td>
<td>Ion implantation</td>
</tr>
<tr>
<td>LEDs</td>
<td>Light-emitting diodes</td>
</tr>
<tr>
<td>LT</td>
<td>Low temperature</td>
</tr>
<tr>
<td>NDE</td>
<td>Non-destructive evaluation</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>PIII</td>
<td>Plasma immersion ion implantation</td>
</tr>
<tr>
<td>PSC</td>
<td>Plasma spray coatings</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluorene</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning acoustic microscopy</td>
</tr>
<tr>
<td>SAW</td>
<td>Surface acoustic wave</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy or electron spectroscopy</td>
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Chapter 1 Introduction

1.1. Application of Ultra Thin Metal Films

Recently corresponding to the growth of the development of material science and technology, the requirements for quality of materials have become more stringent, especially in the aerospace component, microelectronics and medicine fields. It is sometimes difficult for conventional materials to meet these new requirements completely. In this case the use of nanostructured metal films may exhibit useful properties for many advanced applications because of the effects arising from size reduction and large amount of interfaces (Ovid'ko, 2000).

In considering the different applications of deposited thin metal films, (Chow et al., 1982; 2000; Seshan, et al., 2002) the following generic categories can be identified:

1.1.1. Industrial Field

The most important applications of the ultra thin metal films in the field of industry are electronic components, electronic displays, magnetic coatings for data storage, and optical data storage devices.

1.1.1.1. Electronic Components

The fabrication of electronic components, especially solid-state devices and microelectronic integrated circuits, have undoubtedly found the widest and most demanding applications for thin film depositions. These films typically consist of semiconductor materials, dielectric and insulating materials, and metal or refractory metal silicide conductors (Ovid'ko, 2000).

Thin metal films play an important role in the development of electronic devices. Thin metal films deposited at low temperature (LT=77 K) have shown some unique
properties which enhance device performance. An insulating substrate was used for Au, Ag, and Al metal deposition. It was found that all LT thin films become electrically continuous at a much lower thickness than room temperature (RT=300K) films. Electrical measurements determined that the LT films demonstrated several orders of lower resistance compared to very thin (less than 100Å) RT films, which could lead to the potential applications of these films on electronic and optoelectronic devices (Davis, 2003; He, et al., 1996).

Metallic conductors made of thin gold films can function as electrical interconnects in integrated circuits (Li, et al., 2004). Refractory metal nitride coatings find numerous applications in cutting tools, wear resistant parts, and in the jewelry industry. Recent investigations have disclosed interesting applications of thin films of refractory metal nitrides in micro-electronics (Wittmer, 1985).

Tantalum pentoxide thin films can be used as an antireflection coating, insulating layer, gate oxide, corrosion resistant material, and sensitive layer in a wide variety of components, circuits and sensors (Chaneliere, et al., 2006). Solar selective coatings, solar control, photoconductors, solid state and photoelectrochemical solar cells, optical imaging, and hologram recording, are some of the applications of metal films (Mane, et al., 2000). Robotic and medical devices require electrical interconnects that can sustain large and reversible stretching (Lacour, et al., 2005).

1.1.1.2. Electronic Display

Electronic displays are used for interfacing electronic equipment with human operators. Different components and device structures are required, such as liquid-crystal
displays, light-emitting diodes (LEDs), electroluminescent displays, plasma and fluorescent displays, and electrochromic displays.

The fabrication of these displays requires transparent and conductive films, luminescent or fluorescent films as well as dielectric and insulating layers.

1.1.1.3. Magnetic Coatings for Data Storage

Thin films of magnetic materials have found wide commercial applications for data storage in computers and control systems.

1.1.1.4. Optical Data Storage Devices

Thin films are finding increasing commercial use for optical data storage devices in compact disks and computer memory applications.

1.1.2. Medical field

Ultra thin metal films can be used as stent coatings to control the release of medication. The drug to be released in the body is incorporated into the coating (Gertner, et al., 2003). Titanium metal and alloys are widely used as implanted materials. The natural film of titanium oxide formed on titanium surface protects the surface of implants against corrosion. This natural film will transform the surface of the implants into a bioinert material. This means that the implant will not lead to a rejection reaction in the body. There are studies showing that covering the implant with another layer containing calcium and phosphorus provides the surface with a bioactivity property as well as bioinductivity. These qualities are desirable since they will prevent a rejection reaction of implant in the body (Kokubo, et al., 1996; Ignatov, et al., 2003).

Another application of thin metal films in medical field is porous metal coatings deposited on implants to facilitate implant fixation and bone in growth (Davis, 2003;
Devanathan et al., 1994). Secure tissue prosthesis attachment is a vital requirement for the successful performance of most surgical implants. Load bearing orthopedic implants for bone and joint replacement are useful only if the implant can be firmly fixed with the host bone. Porous metal films, polymers (porous polysulfone and polyethylene) and polymer based composites (carbon fiber filled polytetrafluorene, PTFE) were investigated (Davis, 2003), and these led to the current widespread use of porous coated joint replacement implants, principally porous metal films coated hip-and knee joint implants. Porous metal coated implants provide fixation through either cement interlocks with the porous structure or fixation via in growth of the bone tissue. In addition it was shown (Pillar, 2004) that the use of porous metal coating over an implant lead to a decrease of stress shielding and thus to a decrease in bone resorption.

Porous metal thin films for coatings of medical implant devices have to meet new requirements such as highly biocompatible surfaces, which in some cases can support direct on growth of local tissue.

Biocompatibility has been defined as “the ability of a material to perform with an appropriate host response in a specific application” (Williams, 1987; Ratner, 1996; 2001). In other words biocompatibility means that the material, or any leachable products from it, does not cause cell death, chronic inflammation or other impairment of cellular functions.

Other requirements that porous metal thin films have to meet are the following:

- high corrosion resistance
- the ability to be fabricated into structured surfaces, thus allowing optimization of morphology and porosity (of the covered implants) to fit the living recipient tissues,
- to have an elastic modulus closest to that of the tissue of the cortical bone,
- good adhesion (Davis, 2003; William, 1987)
- bioactive, hence inducing bone in growth (Kokubo, et al., 1996; Ignatov, et al., 2003)

In general, the choice of a thin film deposition process is based on a set of material properties to realize the intended purpose.

These parameters are for metal based thin films:

- thermal parameters (expansion coefficient, thermal conductivity, melting point, recrystallization temperature).
- mechanical parameters (intrinsic stress, hardness, elasticity, ductility, adhesion).
- optical parameters (absorption, reflection, spectral characteristics)
- chemical parameters (composition, reactivity, chemical resistance, toxicity and hygroscopicity).
- morphology (crystalline structure, crystalline orientation, kind of defects and defect density, surface topography, structure of interfaces) (Wetzig et al., 2003).

1.2. Deposition of Ultra Thin Metal Films

Thin-film deposition technologies are either purely physical, such as evaporative methods, or purely chemical, such as gas and liquid-phase chemical processes (Maisel et al., 1970; Bunshah, 1982; Ghandi, 1983).

Any property may be influenced by the deposition technique and its parameters. However, each deposition technique has its limitations, but, due to the wide variety of
processes, it is probable that a deposition process can be found and developed for a specific set of thin film properties in most cases.

Some of these methods can be used to deposit ultra thin films only on specific substrates such as: conductive or semiconductive and not on dielectric substrates. This could be a big disadvantage since today a large number of implants are made from dielectric materials (Hench, 1991).

A number of methods for thin films deposition are used in medicine and industry, namely physical vapor deposition, chemical vapor deposition, ion implantation, plasma immersion ion implantation, ion beam assisted deposition, plasma sprayed coating, electrodeposition and electroless deposition are amongst the most widely used.

1.2.1. **Physical Vapour Deposition (PVD)**

There are several techniques used in the deposition of hard coatings. These are called physical vapor deposition technologies or are more commonly referred to as PVD technologies. These technologies are all characterized by changing the state of a solid metal to create a metal vapor. The metal vapor that is created is a mixture of material which is totally or partially ionized, called plasma that can be made to react with different gases to form thin film coatings that are very hard and have exceptional adhesion (Davis, 2003; Freund, 2004).

Since it was introduced to the medical device industry in the late 1980’s, PVD has become widely used to deposit wear resistant thin film coatings on a variety of medical devices, including orthopedic implants, pacemakers, surgical instruments, orthodontic appliances and dental instruments (Davis, 2003).
The most commonly used coatings are TiN, ZrN, AlTiN, CrN and amorphous carbon are being tested as alternative biomedical coatings (Davis, 2003).

Some of the disadvantages of PVD are:
- it is extremely difficult to coat odd shapes and similar surface features.
- the rate of the coating is usually quite slow,
- processes require large amount of heat and appropriate cooling system.
- too much heat desorbs the deposited film, evaporating it away, and high capital cost,
- equipment capabilities limit the process to small and medium sized parts. (Mattox, 1998).

1.2.2. Chemical Vapour Deposition (CVD)

Chemical vapor deposition (CVD) is a materials synthesis process where constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. Many of these CVD reactions have long been used for coating of substrates at reduced pressure, often at high temperatures (Ahlroth et al., 1981, Chow et al, 1982; Seshan, 2002; Wetzig, 2003).

The chemical vapor deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of materials essential to advanced technology, particularly solid-state electronics where some of the most sophisticated purity and composition requirements must be met (Chow et al., 1982; Seshan, 2002; Wetzig, 2003). CVD is a very versatile process used in the production of coatings, powders, and fibers. With CVD, it is possible to produce almost any metallic or
non-metallic element, including carbon and silicon, as well as compounds such as carbides, nitrides, borides, oxides, intermetallics and many others.

Protective coatings are the most common application of CVD. Protective coatings, as their name implies, are deposited onto a part (substrate or mandrel) to provide wear, corrosion and/or erosion protection (Pierson, 1992). Among protective coatings a special attention was paid to biocompatible coatings, and especially to porous coatings which are used to coat medical implants. CVD is a good method of fabricating porous coatings which can be tailored to match the stiffness and strength of bone (Levine et al., 2006).

Some disadvantages of CVD are:

- high temperature of the process, approx. 1000 C
- significant dimensional changes and geometrical distortions
- decarburization of the part top layer, resulting in deep damage to the surface when the coating fails
- loss of part’s hardness (Choy, 2001).

1.2.3. **Ion Implantation (II)**

Ion implantation has been used to form silicon-on-insulator structures by implanting large doses of atomic or molecular oxygen ions into single-crystal silicon substrates to produce a buried oxide layer with well defined interfaces after annealing (Chiu et al., 1984; Kasi et al., 1987; Jethanandani, 1997).

Ion implantation has been used as well for coating biomedical devices, to modify surface properties of materials similar to coating processes, but it does not involve the addition of a layer on the surface (Cui, et al., 1999; Davis, 2003).

Among disadvantages of ion implantation it should be mentioned:
- very deep and very shallow profiles are difficult to be coated
- the coating have high impurity content
- expensive (Andres, 2000; Ziegler, 1992)
- uses extremely toxic gas sources such as arsine (AsH₃) and phosphine (PH₃)
- pre-etch implantation, especially if the substrate is dielectric (damage can occur to the substrate) (Dong et al., 1999)

1.2.4. Plasma Immersion Ion Implantation (PIII)

It is well known that plasma immersion ion implantation and metal (PIII) is especially suited for the formation of a functional surface layer without changing bulk properties. PIII is used to treat the surfaces of solids (metals, ceramics, semiconductors, polymers) for structural or chemical changes, by radiation damage and ion implantation (Cheung, 1996; Mändl et al., 2002; Willmann et al., 2001). The thickness of thin film layers created by PIII is about 1μm, TiN thick enough to withstand a break down even at applied loads of more than 150N. This is very useful for avoiding deformation during loading and unloading in vivo (Willmann et al., 2001). Therefore this method is very attractive for depositing thin film (coatings) on the surface of biomedical implant.

A major drawback of this technique is that it can be used only at limited temperature otherwise; some of the parts of surface of the implant can be degraded at elevated temperatures (Dong et al., 1999). In addition, in the context of obtaining thin metal porous films, which provide an enhanced fixation of implant and facilitate bone in growth, plasma immersion ion implantation is not the best technique to be used since is
well known that this method is used for the production of pore free layers (Conrad et al., 1987; Tendys et al., 1988, Mändl et al., 1996).

1.2.5. Plasma Sprayed Coatings (PSC)

Plasma-assisted deposition of thin films is used widely in microelectronic circuit manufacturing. Plasma processes, are generally used to form films of plasma silicon nitride on semiconductor devices, and to deposit hydrogenated, amorphous silicon layers for thin-film solar cells. Materials deposited include conductors such as tungsten, copper, aluminum, transition-metal silicides, and refractory metals, semiconductors such as gallium arsenide, polycrystalline silicon, and dielectrics such as silicon oxide, silicon nitride, and silicon oxynitride (Cote et al., 1999).

Plasma-sprayed coatings are used in orthopedic medicine. For instance, Besov and Batrak developed a new technology of plasma spraying of a biocompatible porous coating of titanium. The coating was deposited onto the surface of hip joint endoprostheses. This technique produces a strong bond of the hard tissue with the surface of endoprostheses as a consequence of intergrowth of the hard tissue (bone tissue) in the porous skeleton of the coating. It was shown that the strength of the bonding of the implant with the bone depends on both the volume of open porosity as well as the mean dimension of the pores. It is believed that the optimal values for these parameters are in the range 20-40% and 100-400 μm (Besov et al., 2005). Plasma spraying is the current commercial process for depositing hydroxyapatite (HA) coatings on orthopedic implant surfaces. Many researchers have reported problems with plasma sprayed HA coatings including poor coating-metal adhesion, non-uniformity in coating thickness, and
alteration in structural and chemical properties during the coating process, and non-uniformity in coating density (Ong et al., 2006)

1.2.6. Electrodeposition

In electroplating a metallic coating is electrodeposited on the cathode of an electrolytic cell consisting of a positive electrode (anode), a negative electrode (cathode), and an electrolyte solution (containing the metal ions) through which electric current flows. Some of the technological areas in which means and methods of electroplating constitute an essential component are all aspects of electronics: macro and micro, optics, optoelectronics, and sensors of most types, as well as the medicine field, to name only a few (Gertner et al., 2003, Schlesinger, Electrochemistry Encyclopedia, 2002). Furthermore, the ability to deposit very thin multilayer (less than a millionth of a cm thickness) via electroplating represents yet a new avenue of producing new materials.

The basic components for electrodeposition of metals from an aqueous solution are the following: power supply, two metal electrodes (M1 and M2), water containing the dissolved ions, and two metal solution interfaces; M1/solution and M2/solution.

The major disadvantage of electrodeposition is that the deposition can be done only onto conductive substrates.

![Figure 1.2-1 Schematics of an electrolytic cell for plating metal "M" from a solution of the metal salt "MA"](image)

The basic components for electrodeposition of metals from an aqueous solution are the following: power supply, two metal electrodes (M1 and M2), water containing the dissolved ions, and two metal solution interfaces; M1/solution and M2/solution (Schlesinger, Electrochemistry Encyclopedia, 2002)
1.3. Electroless Deposition (ELD)

Special attention was paid to electroless deposition for two reasons: it was the method used in the present investigation for ultra thin film deposition and because of its advantages over the other deposition techniques.

The term “electroless deposition” describes the methods of depositing metals and alloys by means of electrochemical reactions. The chemical deposition of a metal from an aqueous solution of a salt of said metal has an electrochemical mechanism, both oxidation and reduction (redox) reactions involving the transfer of electrons between reacting chemical species (Mallory et al., 1990; Schlesinger et al., 2000).

The benefits of electrochemically (and specially electroless) deposition applications (coatings) in medical implants as well as in industry are significant. For instance, electroless technique offers the opportunity of coating even on smooth and odd shape surfaces, a very important feature for both the medical and industrial fields.

The advantages of electroless plating are:

- electric power supplies are not required
- a functional layer is deposited
- non conductive materials are metallized
- a uniform layer is deposited even on complex shapes
- the coatings provide better corrosion resistance than some of the other deposition techniques
- the equipment for electroless plating is simple and cheaper than the equipment for other techniques
the chemical and physical properties of the coating can be easily controlled are more reproducible and environmentally safe than other techniques.

1.3.1. The General Principle of Electroless Deposition

Electroless deposition (ELD) of metals is based on the deposition and reduction of metallic ions from a solution to a surface in the absence of an external electric current source. This deposition requires the immersion of a surface catalytically activated in a plating bath containing complex metal ions and a reducing agent. This bath needs careful control with respect to its chemistry, stirring, temperature, and pH for reliable and high-quality deposits.

ELD proceeds after its initiation on the surface via autocatalysis and uses the reducing agent from the solution as a source of electrons. Many parameters can affect the ELD of metals, such as the density of the catalyst and its degree of activity on the surface, the adhesion of the deposit to the substrate, and the composition and conditions of the plating bath. Understanding the chemical reactions in ELD requires insight into the chemical and physical state of the catalytic interface, which can only be addressed using a restrictive scope of instrumentation. ELD is nevertheless a remarkable method to metallize substrates. It is proving increasingly useful in semiconductor and packaging technologies, for example.

In order to better understand the electroless deposition process it should be mentioned that electroless deposition is like a specific case of electrodeposition (Paunovic et al., 1998). There are only a few differences that could be seen in a comparison between electrodeposition and electroless deposition.
The basic components for electrodeposition of metals from an aqueous solution are as shown in Figure 1.2-1, power supply, two metal electrodes (M1 and M2), water containing the dissolved ions, and two metal solution interfaces; M1/solution and M2/solution.

Electrolytic cells for electroless deposition and for electrodeposition are shown in figure 1.3-1. A first difference that could be noticed is that for electroless deposition there is no power supply and the electrolytic cell has only one electrode. However the solution is more complex. It contains water, a metal salt MA (M\textsuperscript{2+}; A\textsuperscript{-}), and a reducing agent Red as basic components.

Another difference between the two processes is given by the electron source. In electroless deposition the electrons are supplied by the absorbed reducing agent and in electrodeposition they are supplied by an external power source. Due to the two different electron sources in the electrodeposition process the coating can be deposited only on conductive substrates. On the contrary in an electroless system there are two types of substrates: conducting and insulating (dielectric) catalytic substrates. Another major difference prior to performing ELD is the seed (the placement and activation of the catalyst on the surface).

In spite of all differences it is widely accepted that autocatalytic plating, (which is the formally adopted name for electroless deposition), proceeds along the electrochemical mechanism as a simultaneous reaction of the cathodic metal deposition and anodic oxidation of the absorbed reducing agent on the catalytic substrate. Moreover, electroless plating could be considered as a particular case of electrodeposition (Paunovic et al., 1998; Schlesinger et al., 2000).
Figure 1.3-1  Electrodeposition versus Electroless Deposition
In electrodeposition, there are two electrodes: a cathode and an anode, where two separate redox reaction take place, while for electroless deposition both redox reaction occur only on the surface of the object to be coated due to the catalytic nature of the surface. In electroless deposition process it is only one electrode, where both the anodic and the cathodic reactions take place (Schlesinger et al., 2000).

1.3.2.  Activation of Dielectric Substrates

Dielectric substrates (i.e., noncatalytic substrates) have to be activated before the electroless deposition. One of the major types of activation method is electrochemical activation. This method is used to generate catalytic nuclei of metal M on the surface of the dielectric (noncatalytic) substrate. The catalytic nuclei of metals may be generated in an oxidation reduction reaction:

\[ M^{n+} + \text{Red} \rightarrow M + \text{Ox}, \]

where: M \(^{n+}\) is the metallic ion, Red is the reducing agent, M is the metal catalyst and Ox is the oxidizing agent.

Usually the preferred catalyst is Pd and thus the preferred nucleating agent is Pd \(^{2+}\) (from PdCl\(_2\)). The preferred reducing agent Red in this case is Sn \(^{2+}\) (from SnCl\(_2\)). In this case the overall reaction is:

\[ \text{Sn}^{2+} + \text{Pd}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pd} \]
Sn\(^{2+}\) can reduce Pd\(^{2+}\) ions since the standard oxidation–reduction potential of Sn\(^{4+}/\text{Sn}^{2+}\) is
0.15 V and that of Pd\(^{2+}/\text{Pd}\) is 0.987 V. The flow of electrons is from a more
electronegative couple (Sn\(^{4+}/\text{Sn}^{2+}\)) toward a less electronegative couple (Pd\(^{2+}/\text{Pd}\)).

Electrochemical activation using PdCl\(_2\) and SnCl\(_2\) may be performed in either two
steps or one (Paunovic et al., 1998; Touyeras et al., 2005).

In the one step activation process the involved reactions are:

\[
\begin{align*}
\text{Sn}^{2+} + \text{Pd}^{2+} + 4\text{Cl}^- &\rightarrow \text{Sn}^{2+} + (\text{PdCl}_4)^{2-} \\
\text{Sn}^{2+} + \text{Pd}^{2+} &\rightarrow \text{Sn}^{4+} + \text{Pd}
\end{align*}
\]

In this activation process the sensitizing and activating (nucleating) solutions are
combined. This solution contains various Sn-Pd chloride complexes. These complexes
may subsequently transform into colloidal particles of metallic palladium or a metallic
alloy (Sn/Pd) to form a colloidal dispersion. This dispersion may be unstable.
Stabilization is possible using an excess of Sn\(^{4+}\) ions. Once the dispersion is stabilized, Pd
particles are absorbed on the dielectric surface and surrounded by Sn\(^{4+}\) ions. In order for
Pd to become available for plating Sn\(^{4+}\) ions should be removed by solubilization. The
solubilization solution is a mixture either of fluoroboric and oxalic acids in a dilute
solution or NaOH or HCl (Paunovic et al., 1998; Touyeras et al., 2005). After
solubilization Pd is available for deposition forming catalytic sites on the substrate.
Figure 1.3-2  The dissolution of tin palladium agglomerates in activation.
In activation sensitization step Sn-Pd complexes are formed. These complexes may transform into colloidal particles of metallic palladium or metallic alloy (Sn/Pd) to form an unstable colloidal dispersion (Touyeras et al., 2005).

The other method, two steps activation, has as the name suggests two steps: 1) sensitizing; 2) activating.

1) During sensitization, active sites are produced by dipping the substrate in a reductive solution. SnCl₂ is a sensitizer because it favors nucleation and inlay of precious metallic catalyst particles. Some tin in a metallic form is added to the sensitizer solution in order to avoid direct transformation of divalent tin ions into tetravalent tin.

2) The activation step consists of providing catalysts. A typical catalyzing (nucleating) solution contains (PdCl₂ and HCl). The substrate is immersed in a bath containing precious metal ions (palladium ions) and the global reaction is:

\[
\text{Sn}^{2+} + \text{Pd}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pd} \quad (\text{Paunovic et al., 1998; Touyeras et al., 2005}).
\]

1.3.3. Electroless Deposition of Ni (EN)

Currently, electroless nickel plating (EN) is no doubt the most important catalytic plating process in use. Electroless nickel is widely used in the chemical process industry, for storage and transportation of chemicals. To ensure continued growth, the industry has actively sought methods of reducing the cost of storage, manufacture and transportation
of chemical products. In turn the search has resulted in increased demand for electroless nickel and implementation of standards, which have improved the reliability of the performance of construction materials (Krishnan et al., 2006).

Requirements for materials used in the chemical process industry include a need to maintain product purity, to prevent corrosion/erosion problems that may affect the environment and to optimize cost and service life of equipment.

The principal reasons for the commercial and industrial widespread of electroless nickel are due to the unique properties of the electroless nickel deposits.

Electroless nickel has excellent corrosion resistance, is not susceptible to stress corrosion cracking and can be deposited with a range of composition for use in acidic, neutral or alkaline conditions (Krishnan et al., 2006).

Typically, the constituents of an EN solution are:

- a source of nickel ions
- a reducing agent
- suitable complexing agents
- stabilizers/inhibitors (Agarwala et al., 2006)

1.3.3.1 The nickel source

Nickel sulfate is well known as the preferred source of nickel cations. Other nickel salts, such as nickel chloride and nickel acetate, are used for very limited applications. When compared to nickel sulfate, the nickel acetate does not yield to any significant improvements in bath performance. The ideal source of nickel ions is the nickel salt of hypophosphorus acid, Ni(H₂PO₂)₂. The use of nickel hypophosphite would

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eliminate the addition of sulfate anions and keep to a minimum the buildup of alkali metal ions while replenishing the reactants consumed during metal deposition.

1.3.3.2. Reducing agents

Four reducing agents may be used in the chemical reduction of nickel from aqueous solutions: sodium hypophosphite, sodium borohydride (BH), dimethylamine borane (DMAB), and hydrazine. However, in the present research project the experiments for obtaining Ni thin films were carried out using only one of the above mentioned reducing agents, sodium hypophosphite. The hypophosphite ion is used as a reducing agent because the oxidation reaction of the hypophosphite ion is possible on Ni surface (Mallory et al., 1990).

1.3.3.3. Complexing Agents

The additives referred to as complexing agents in electroless nickel plating solutions are, with two exceptions, organic acids or their salts.

Complexing agents perform four principal functions in the electroless nickel plating bath:

- Maintaining the pH of the bath at a constant value; they act as buffers
- Preventing the precipitation of nickel salts, e.g., basic salts or phosphites
- Reducing the concentration of nickel free ions
- They influenced directly the deposition reaction and hence the nickel deposit.

The two exceptions among the complexing agent which are not organic acids or their salts are the inorganic pyrophosphate anion, and the ammonium ion, which is usually added to the plating bath for pH control or maintenance. Both of them are used only in alkaline solutions (Mallory et al., 1990).
1.3.3.4 Stabilizers

The role of stabilizers is to protect the electroless deposition bath against decomposition. The stabilizers prevent the increase in the volume of hydrogen evolved and also the formation of the precipitate through the solution events that usually precede bath decomposition (Schlesinger et al., 2000).

1.4. Nickel (Ni) and Cobalt (Co) in Ultra Thin Films

A large variety of metals are used for ultra thin metal films used as coatings in industry and medicine (Siewenie et al., 1999; Davis, 2003). For example, metal silicide thin films are integral parts of all microelectronics devices (Poate et al., 1978).

Electroless nickel-phosphorus (Ni–P) alloy coatings have been widely used in many industrial sectors. For many applications, the most important properties are high hardness, good wear corrosion resistance, and uniform thickness (Sohn et al., 2004) Nickel thin films have numerous applications in the aerospace, automotive, and textile industries. Electronics and electrical devices are other applications of these films (Agarwala et al., 2006; Krishnan et al., 2006).

Electroless cobalt-phosphorus (Co-P) films are interesting primarily due to their magnetic properties. Therefore, the relationships among the magnetic properties, the plating variables, and the microstructures of the electroless Co-P film have been studied extensively (Liu et al., 2004).

To extend the range of electroless nickel coating applications in industry, it was necessary to develop ternary or quaternary alloy deposits, like Ni-Co-P (Younan et al., 2002).
Electroless Co–Ni–P alloy films were studied for their use as a thin film magnetic recording media (Sankara Narayan et al., 2003).

In medicine Ni-Ti alloy was widely used. Ni-Ti thin films shape memory alloy appeared to the medical market in the 1980’s and their global market were more than 130 billions in 2002. In most medical applications materials must be biocompatible. Ni-Ti offers the body temperature activated shape memory effect (SME) and super elasticity (SE). These characteristics can be used in medical devices. Dental arch wires and stents for example are benefiting from SE. Ni-Ti is used for dental implants and the attachment of partial dentures and for orthopedics. In the latter, one of the main applications are clamps for connecting bone fractures (Trepanier et al., 1998; Hannula et al., 2006).

There were some concerns regarding the biocompatibility of nitinol thin films. Most of the tests conducted to study its biocompatibility, have led to the conclusion that Ni-Ti is a very good candidate as a biocompatible material (Rondeli et al., 1999; Arndt et al., 2005; Es-Souni et al., 2005). Only one study attributes moderate cytotoxicity to Ni-Ti, which has been found to be comparable to that of Co–Cr–Mo based (Dinca et al., 2006).

The reason for choosing nickel in our research is due to its high corrosion resistance. Corrosion resistance is a very important feature for coatings of biomedical implants, drug delivery devices and also for coatings used in industry.

On the other hand cobalt alloys do not offer such good corrosion resistance, but they are not toxic. A very well known use of the Co based alloy is in medicine, especially in medical implants due to their good biocompatibility (Endres et al., 2004; Es-Souni et al., 2005; Baldvin et al., 2006; Numata et al., 2006).
The idea of using nickel and cobalt seems meaningful since combining the two elements it could eventually obtain a thin film combining both high corrosion resistance of Ni and non toxicity property of Co.

1.4.1. The Use of a Dielectric Substrate

In the present investigation it was found useful to work with a dielectric substrate such as glass, as a support for ultra thin films. The reasons for choosing glass (as a model substrate) are the following:

- glass is dielectric
- is bioinert
- among the others nominated dielectric substrates, glass is more available.
- coating of metal thin films on ceramic materials is very important for electronic, aerospace, energetic industries

The benefits of working with dielectric substrates are the following:

- nowadays many hip implant components or knee implant components are made of ceramic material (dielectric substrate) rather than a metal or polyethylene (Ayers et al., 2006; Murphy et al., 2006; Petit et al., 2006).
- the natural electrophysiological conditions (as negative biopotentials) of bones are preserved and the healing period is shortened
- a stable osteosynthesis is achieved when using dielectric implants (Andrew et al., 1962; Dobrev et al., 1984; Neumann et al., 2006).
- implants should mimic as well as possible the bone structure and bone is dielectric (Sierpowska et al., 2006).
1.5. Quality Evaluation of Ultra Thin Metal Films

Defects within the structure (i.e., inclusions, delaminations, disbonds, cracks and micro cracks) negatively affect the properties of metal films deposited electrochemically or by any of the many methods of film production. A number of microscopic and spectroscopic methods are available for microstructure evaluation. Frequently employed testing methods include: optical absorption and/or emission spectra, light (photons), electron, ion, or atom scattering, visual inspection, optical, electron-transmission and scanning electron microscopy, X-ray, and IR-radiometry that records variations in heat absorption or emission to name a few. Optical and electron microscopy methods do have adequate resolution but, the sample preparation is crucial and often the most difficult part of the characterization operation. Those methods include staining or contrasting, etching, etc (Paunovic et al., 1998; Miyasaka et al., 2002). Some of the most known surface analysis techniques will be very briefly mentioned together with a background of scanning acoustic microscopy, which was the method applied in the present research project for quality evaluation of Ni-Co ultra thin films.

1.5.1. Surface Analysis Techniques:

It has been shown (Mittal, 1993; Paunovic et al., 1998) that it is possible to group the analysis techniques for the characterization of thin films into following categories:

1. Mass–spectrometric techniques

2. Optical techniques

3. Other techniques

The most important method among mass-spectrometric techniques is: secondary-ion mass spectrometry (SIMS).
This technique is used to determine the quantitative elemental or isotopic composition of the surface of a thin film. SIMS is the most sensitive surface analysis technique, but is more difficult to accurately quantify than some other techniques.

Evaluating coated materials, thin films, metal alloys, data showing material characteristics can be collected using optical microscopes and scanning electron microscopes and through destructive tests such as: pull, compression, bending, torsion, corrosion etc. Over the years a wide range of film characterization and evaluation procedures have been developed (Mittal, 1976; 1993; Miyasaka et al., 2002; Maeva et al., 2004).

An example of a technique from the third group is scanning tunneling microscopy. This technique provides a picture of the atomic arrangement of a surface by sensing corrugations in the electron density of the surface that arise from the positions of surface atoms.

All these methods are analyzing the surface of thin films. However, in the context of evaluating ultra thin films systems, some defects such as delaminations, micro cracks and the like are often present at the interior of the system. Therefore, a non destructive method such as scanning acoustic microscopy (SAM) is very useful for quality evaluation of the thin films and also the interface film-substrate.

1.5.2.  High Frequency Acoustical Imaging in the Investigation of Ultra Thin Metal Films

At the present time the development of material science and technology corresponds to a growth of requirements for quality assurance, especially in aerospace components, microelectronics and medicine. Generally speaking when a new material (composite
material, coated material, thin film and metal alloy) is evaluated, tests for life estimation, quality, and safety analyses are prepared (Parthasarathi et al., 1997; Miyasaka et al., 2002). Typically, data showing material characteristics are collected by an optical microscope and scanning electron microscope and through destructive test such as pull, compression, bending, torsion, fatigue, impact and corrosion. However, critical defects such as voids, delaminations, and debonding sites of the thin films often exist in the interior. Therefore, conventional microscopes cannot observe them directly (Miyasaka et al., 2002). Hence, defects must be exposed by cutting or grinding the specimens in layers which poses the following problems:

- the defects might be changed when cutting and polishing the specimens.
- it might be possible that not all defects will be exposed.
- some specimens are difficult to cut or grind.
- when the size of the defects is less than 10 μm, it is difficult to see their three dimensional distribution by grinding in layers (Miyasaka et al., 2002)

Scanning acoustic microscopy (SAM) is a very practical, non destructive technique, which can be used for quality evaluation of thin metal films, in the industrial and biomedical fields. Therefore, the development of improved techniques for evaluating the quality of adhesion was of critical importance to thin metal films. It has been shown that over the years a wide range of film characterization and evaluation procedures have been developed. There are over 200 mechanical testing techniques for the characterization of film adhesion. Most currently utilized mechanical testing techniques are empirical in nature, and often do not provide direct correlation between test results and film
performance (Mittal, 1976; Parthasarathi et al., 1997; Maeva et al., 2004). Taken into account that different test, are performed by individual laboratories under different conditions, little room is given for comparison of test results. Many researchers had a general consensus that a standardization of film evaluation technique is needed (Mittal, 1976; 1993).

Mittal suggested a list of the desirable features of a good evaluation technique for measuring the adhesion properties of films. The features are the following:

- Non-destructive
- Quantitative
- Reproducible
- Quick
- Adaptable to routine testing
- Simple
- Objective
- Applicable to a wide range of films and substrates (Mittal, 1993).

1.5.2.1. Internal Imaging of Thin Films

From all non-destructive evaluation techniques, scanning acoustic microscopy (SAM) satisfies most of the previously identified requirement and prevents the majority of problems posed by the other techniques. The scanning acoustic microscope uses ultrasound to produce enlarged images of the microscopic structures of materials. The operating principle of the scanning acoustic microscope is based on the interaction of high frequency acoustic waves with the object that is subjected to ultrasound. Any interface between two materials whose acoustic impedance is different (defined as the
product of density and acoustic wave velocity) provides a contrast mechanism which can be imaged (Parthasarathi et al., 1998). Practically the scanning acoustic microscope is an instrument that subjects an object to ultrasound and detects the variations of the elastic properties of the object. The elastic properties are determined by the molecular arrangement of the material, molecule size, and intermolecular force.

Wegelein and Wilson found that the variation of contrast which appear in acoustical pictures is unique to the material being studied (Wegelein et al., 1977). Each material has its unique characteristics. Accordingly, each objects reacts in its own peculiar way when it is examined with ultrasonic waves. The waves received from the object can be converted into an image. Moreover, due to the fact that ultrasonic waves can penetrate into an object's interior, not only the surface, but even the sub surface and the interior of evaluated specimen can be visualized (Briggs, 1992).

In the context of evaluating opaque objects non-destructively, and of obtaining the acoustic characteristics of specimens (such as ultra thin metal films), it has been very popular to visualize their internal structures by instruments using the basic features of ultrasound waves (reflection, transmission, refraction, and diffraction). However, the frequencies for these instruments have been in the range from 20 kHz to 10 MHz, limiting the resolution of the process. Furthermore, most of their transducers do not have features to focus ultrasound so that the diameters of the ultrasonic beams would be small enough to form an image that has the resolution and/or the contrast of optical microscopes. In addition traditional ultrasonic imaging cannot provide data on the elasticity of a small area of a specimen (Briggs, 1992).
Therefore, scanning acoustic microscopy is a viable non destructive method that has high resolution defect visualization to determine elastic properties of various types of samples. In addition, the contrast mechanism of the SAM depends on the reflection function, and the topology of specimen (smooth or surface with discontinuities such as crack, steps, joint interface) from objects that have different acoustic properties and thus the chemical agents for staining and etching the metal thin films are not necessary in order to clearly observe the defect on the interfaces. Because the beam is focused (up to sub micrometer size) and has high frequency (100 MHz to 2 GHz), the resolution of the system is of the order of optical microscope. Regarding image formation, the SAM can detect the amplitude and the phase of a reflected wave. By analyzing them, the elastic properties of a specimen can be quantitatively and qualitatively determined (Yu et al., 1995).

1.5.2.2. Quality Evaluation of Thin Films

One of the main problems affecting the performance of thin metal films in all applications is their adhesion (Maeva et al., 2004; Hu et al., 2006)

In the context of ultra thin films, one can appreciate the acute need for developing suitable non-destructive evaluation (NDE) technique to characterize coating/thin film adhesion and properties. This NDE technique should satisfy all the requirements for a good evaluation technique and should be able to provide reproducible quantitative information on the adhesion properties of films (Parthasarathi et al., 1997; Maeva et al., 2004). Parthasarathi, Tittmann, and Nishida characterized metal thin films interface integrity and adhesion to the substrate through scanning acoustic microscopy (Parthasarathi et al., 1997; 1998). They used scanning acoustic microscopy as a reliable
NDE technique for thin film evaluation. They proved that the scanning acoustic microscope (SAM) is an effective tool for the characterization of thin film/substrate interface integrity as well as nondestructive subsurface imaging. They have also shown that the potential offered by the SAM is an important tool to be used in conjunction with indentation/fracture mechanics based studies of thin film adhesion. In order to visualize the defects in thin films they used scanning mode of the microscope. In the scanning mode of the microscope the scanned image is formed as a result of interaction between acoustic waves and the material being studied. Parthasarathi et al presented the application of innovative SAM based imaging techniques for the assessment of film integrity and damage in titanium nitride and polycrystalline diamond thin films (Parthasarathi et al., 1998). Using scanning acoustic microscopy they made a qualitative characterization of thin films: TiN: 3.1-3.4 μm thick, obtained by PVD and CVD diamond 5μm thick. In order to study the adhesion of the polycrystalline diamond films and titanium nitride films they simulated damage or in other words they used destructive adhesion techniques to cause interfacial damage. The purpose of these simulations was to study the potential offered by scanning acoustic microscope (SAM) for the non-destructive, qualitative characterization of interface integrity of thin films. Martin Hoppe and Jürgen Bereiter-Hahn shown that detecting defects as delamination due to the poor adhesion of thin films is one of the “classical” applications of scanning acoustic microscopy (Hoppe et al., 1985). Both the acoustic microscope's penetration ability and the ability to reveal mechanical properties are needed. Hoppe and Bereiter-Hahn have given a typical example of detecting poor adhesion of thin films. They assessed the quality of adhesion of a partly delaminated perm alloy film (thickness 1.5μm) on a crown
glass substrate. They used both optical and acoustical microscopes for quality evaluation of the thin films. In optical pictures only the surface of thin films could be visualized. Acoustical pictures show clearly the delamination area. In their article Hoppe and Bereiter Hahn have shown that delamination and adhesion problems are of a great interest for integrated circuits. Moreover, they have shown that even the crystal defects can be observed using scanning acoustic microscope due to the Rayleigh wave interaction.

1.5.2.3 V (z) Curve

The V (z) curve is defined as the amplitude of the transducer voltage V as a function of lens-to-sample spacing on z axis. The variation in the image contrast due to the changes in the distances between the lens and the sample surface is known as the V (z) effect.

The acoustic microscope can be utilized to generate and detect Rayleigh waves (two-dimensional surface waves). The energy of these waves being confined to a thin surface layer makes them ideally suited for thin film characterization. However, acoustic microscopy for quantitative thin (sub-micrometer) film interfacial strength characterization has been relatively unexplored. Previous efforts include the development of acoustic microscopy techniques for the characterization of thickness and elastic properties of metal thin films. Again, most of these measurements have been made at frequencies in the range 200-300 MHz. These techniques have not been applied at high frequencies (above 300 MHz) for the characterization of thin (sub-micrometer) films (Parthasarathi et al., 1997).
Parthasarathi, Tittmann, and Ianno claimed also that scanning acoustic microscopy using Rayleigh waves can be used for both quantitative and qualitative characterization of thin films (Parthasarathi et al., 1997). Based on the previous experience that the image contrast is very sensitive to changes in the distance between the lens and the sample surface, they studied effect of V (z) curve on the image formation. It has been noticed that moving the lens on z axis toward the sample lead to a change of contrast in the image-V (z) response. V (z) response is caused due to the generation and propagation of surface acoustic wave-(SAW) at the liquid/solid interface.

Using an acoustic microscope (200MHz and lenses focused z=0) they obtained images of laser induced spallation damage in TiN film. Using a higher frequency they showed a high magnification image of a large delaminated area. Parthasarathi et al used an innovative imaging technique: vertical cross sectional imaging. This technique was used to generate vertical cross sectional images of disbonds in thin films. Parthasarathi et al claimed that this procedure is similar to a conventional B-scan however there are some differences. The lens was focused at first at the surface and then was moved in the vertical direction z axis and the same procedure as in the x axis was repeated. The reflected acoustic signal was stored at each point. Vertical cross sectional imaging was found to be a manifestation of the V (z) response to the material. Z scan is affected by Rayleigh wave propagation and hence the V (z) response of the material. Parthasarathi et al showed that through this technique the region of disbond of the surrounding indentation can be measured (Parthasarathi et al., 1997; Parthasarathi et al., 1998). Achenbach showed as well that the V (z) measurement acoustic microscopy provides a
very suitable technique for the quantitative nondestructive determination of thin-film (1μm) elastic constants and the bond quality at interfaces (Achenbach, 2004).

In the context of ultra thin metal evaluation it is not very clear if SAM is a good method for internal imaging and for qualitative and quantitative analysis. All the studies presented above made it clear that SAM is a reliable method for thin metal film evaluation, without providing information about the ability of this method to analyze ultra thin metal films. Moreover, due to the fact the thickness of the film is smaller than the wavelength of acoustic waves even at high frequencies make evaluation of ultra thin metal films a very challenging task. Therefore, in the present investigation the interest was to determine whether SAM was a suitable method for quality evaluation of ultra thin metal films.
1.6. Study Objectives

1.6.1. To determine if a porous ultra thin nickel-cobalt film can be obtained by electroless deposition

We deposit nickel, cobalt and nickel-cobalt ultra thin films on dielectric substrate using the electroless deposition and evaluate their porosity using a complementary NDE technique, namely scanning acoustic microscopy.

1.6.2. To evaluate the quality of nickel cobalt ultra thin films grown on a dielectric substrate using a non destructive method (i.e., scanning acoustic microscopy (SAM))

The main goal of the research is to investigate whether a non destructive method (SAM) is suitable for quality evaluation of ultra thin metal films and if the deposited films have porosity, adhesion, micro-cracks and delamination. It was aimed to experimentally prove using comparisons with the optical microscope that SAM is a good method for quality evaluation of ultra thin film systems.

Since the thickness of ultra thin films (100-120nm) is less than the wavelength of acoustic waves, we propose that defocusing the acoustic lens toward the substrate can generate a surface acoustic wave (SAW). This SAW will enable us to observe the adhesion problems at the interface. SAW is very sensitive to discontinuities in the interface and enhances the contrast of the image. Operating at high frequencies such as 600 MHz and 1 GHz empowers us to achieve an improvement in the quality of the images by enhancing the contrast.
Chapter 2  Materials and Instrumentation

2.1. Materials and Reagents

All reagents were of analytical grade, and used without further purification. The reagents used were: nickel(II) sulfate, cobalt(II) sulfate, sodium hypophosphite, sodium citrate, Rochelle salt, ammonium chloride, ammonium sulfate, stannous(II) chloride palladium(II) chloride (Sigma Aldrich, Mississauga, ON, Canada) Hydrochloric acid (University of Windsor, Chemical Control Centre), NaOH, sodium hydroxide (University of Windsor, Chemical Control Centre, 10M ammonium hydroxide (Fisher Chemicals).

The solutions were prepared using distilled water. The desired temperature of solutions was obtained using a hotplate/ magnetic stirrer with aluminum top (model 700 advanced VWR International Ltd, Mississauga, ON, Canada)with temperature range: 5 to 400°C, speed range 60-1600 rpm.

The desired pH for obtaining the Ni, Co and Ni-Co thin films was measured using Orion PerpHecT Benchtop pH /mV(ORP)/Temperature Meter(Model 320). The pH electrode used was Orion 9202 BN- PerpHect Ag/AgCl, general Combination Glass Electrode (VWR International Ltd, Mississauga, ON, Canada).pH range 0-14.Temperature range 0-100°C. Probe length and diameter 120 mm x 12 mm.

The electrode was prepared before measuring the pH of the metallizing solution as follows. For filling the electrode, Internal Filling Solution -4M KCL saturated with AgCl, Orion 900011 was used. The pH electrode was soaked in pH electrode storage solution Orion 910001 for one hour. Rubbing or wiping the electrode was avoided to reduce the chance of error due to polarization. For short term storage the electrode was soaked in
pH Electrode storage Solution, Orion 910001. All these operations were performed in order to assure the accuracy of measurements.

Fresh buffers were used for calibration. The buffers were chosen not to be more than 3 units apart in pH. Between measurements, electrodes was rinsed with distilled water and placed in the next solution to be measured. All buffers and samples were stirred. A piece of Styrofoam (insulating material) was placed between the magnetic stirrer and the beaker to prevent error from the transfer of heat to the samples. Before measuring the pH for the metallizing solution, in order to get an accurate pH value a two point calibration was performed using fresh buffers. Before calibration all buffers were checked to ensure that they had the same temperature. Samples were also checked to be at the same temperature as the buffers. This step was very important due to the fact that the most common cause of error in pH measurements is temperature. Two buffer calibration was performed using buffers that bracket the expected sample range. Calibration was performed at the beginning of each day, when the pH of metallizing solution was measured. For maximum accuracy, a one –buffer calibration was performed every two hours using a fresh aliquot of pH 7.00 buffer. Buffers used for calibration: Buffer Solution Red-pH 4.00, Buffer Solution Yellow pH 7.00, Buffer Solution Blue pH 10.00 (VWR International Ltd, Missisauga, ON, Canada). In between measurements electrodes were soaked in 0.1 M HCl for half an hour. After the cleaning procedure, electrodes were soaked in storage solution for at least one hour.

The thin films were deposited on glass precleaned microscope slides (University of Windsor, Biology Stock Room). The precleaned slides were used because in the process of electoless deposition the cleaning of the substrate is very important for the film quality
2.2. Instrumentation

The optical pictures of Ni, Co and Ni-Co ultra thin films were taken using a reflection light microscope (Leica DM IRB, Germany) with 200X magnification.

The acoustical pictures of Ni, Co and Ni-Co thin films were taken using the scanning acoustic microscopes for high resolution measurements, Leitz ELSAM (manufactured by LEITZ. Gmbh, Germany). and UH3 Olympus at (1 GHz and 600 MHz)

![Image of scanning acoustic microscope](image_url)

Figure 2.2-1 UH 3Olympus scanning acoustic microscope
The set up for taking the acoustical pictures using scanning acoustic microscope at 600 MHz. Resolution under 1 mkm scanning area 1 x 1 mm. Frequency range: 10 MHz -2.3 GHz (Courtesy of Dr. Miyasaka).
Figure 2.2-2  Leitz ELSAM scanning acoustic microscope
The set up for taking the acoustical pictures using scanning acoustic microscope at 1GHz. ELSAM has a frequency range 100 MHz-2 GHz, six magnification selection, with a maximum resolution of 1μm. It can operate both as an optical reflection microscope. The microscope produces 512x512 pixels images with a scan area starting from 0.8x0.8mm down to 40x40μm.
Chapter 3  Methods

3.1. The basic steps for Electroless Deposition

The basic steps of electroless deposition process are rinsing, sensitizing and catalyzing the substrate and after all these steps are performed the substrate is immersed in metallizing solution.

Figure 3.1-1  Steps of electroless deposition
Overview of a schematic representation of the electroless deposition process for Ni, Co and Ni-Co.

3.2. Sample preparation for Electroless Ni Deposition

3.2.1. Surface Modification of the Substrate

In order for electroless deposition to take place onto a substrate, the surface of the substrate should be modified. Modifying of the substrate requires cleaning and sensitization.
and catalyzing the substrate. Cleaning of the substrate (glass) was achieved by rinsing it with distilled water. The process of seeding catalytic sites was achieved through the two step process of sensitization and activation. For sensitization a solution made of one ml of stock solution (Sn Cl₂ and HCL) dissolved in 200 ml distilled water was used.

Preparation of Sensitizer Solution:

| Table 3.2-1  The composition of sensitizer solution |
|-------------|--------|---------|
| Stock Solution | SnCl₂   | 10 g    |
|               | HCl     | 10 ml   |
| Working Solution | Stock Solution | 1 ml    |
|                | Distilled Water | 200 ml  |

During sensitization, active sites are produced by dipping the substrate in a reductive solution.

Preparation of Activator Solution:

| Table 3.2-2  The composition of activator solution |
|-------------|--------|---------|
| Stock Solution | PdCl₂  | 10 g    |
|               | HCl    | 10 ml   |
| Working Solution | Stock Solution | 1 ml    |
|                 | Distilled Water | 200 ml  |

The activation step consists of providing catalysts. The substrate was immersed in a bath containing precious metal ions (usually palladium ions). Rinsing between steps is very important and it was executed after sensitization, and after catalyzing.
3.2.2. Preparation of Metallizing Solution:

Electroless Ni deposition can be realized using an acidic metallizing bath or a basic metallizing bath. For the present samples an acidic bath has been used for Ni deposition and an alkaline bath has been used for Co and Ni-Co deposition.

The factors that affect electroless Ni deposition rate are temperature and pH.

<table>
<thead>
<tr>
<th>Metallizing solution</th>
<th>Ni (g/l)</th>
<th>Co (g/l)</th>
<th>Ni-Co (65% Ni)g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate, Ni SO₄·6H₂O</td>
<td>30</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Cobalt sulfate, Co SO₄·7H₂O</td>
<td>-</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Sodium hypophosphite, NaH₂PO₂·H₂O</td>
<td>10.6</td>
<td>20</td>
<td>5-40</td>
</tr>
<tr>
<td>Sodium citrate, Na₃C₆H₇O₇·2H₂O</td>
<td>100</td>
<td>100</td>
<td>35</td>
</tr>
<tr>
<td>Rochelle salt, NaK₂C₆H₄O₆·4H₂O</td>
<td>-</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>Ammonium chloride, NH₄Cl</td>
<td>53.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium sulfate, (NH₄)₂SO₄</td>
<td>-</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The composition of metallizing solution for Ni, Co and Ni-Co ultra thin film using electroless deposition technique. Temperature is influencing the rate of deposition as can be seen for the tables below:
Table 3.2-4 Acidic metallizing bath for Ni deposition

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion Time in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizer</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec.</td>
</tr>
<tr>
<td>Activator</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec</td>
</tr>
<tr>
<td>Ni metallizing</td>
<td></td>
</tr>
<tr>
<td>pH= 5.3</td>
<td>300 sec</td>
</tr>
<tr>
<td>t= 53°C.</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2-5 The influence of temperature on plating rate at a constant pH

<table>
<thead>
<tr>
<th>pH</th>
<th>T°C</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>65</td>
<td>Using the same steps for electroless deposition the work was done at different temperatures.</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>The plating rate increases exponentially with the increase in the temperature. The quality of deposited films improved with the increase in temperature.</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2-6 Acidic metallizing bath at pH 4.0

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion Time in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizer</td>
<td>1 min</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec.</td>
</tr>
<tr>
<td>Activator</td>
<td>1 min</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec</td>
</tr>
</tbody>
</table>
Table 3.2-7  The influence of pH on plating rate

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>pH</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>4.4</td>
<td>Using the same steps for electroless deposition the work was done at different pH.</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>The plating rate increases exponentially with the increase in the temperature. The quality of deposited films improved with the increase in pH.</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>

If the pH is allowed to drop too far, (pH< 4) a very low plating rate is observed. The quality of the thin Ni film is also influenced by the decrease in pH (Mallory et al., 1990; Schlesinger et al., 1998; Agarwala et al., 2006). Stirring rate is another important factor besides temperature and pH. The composition of the solution should be maintained constant, meaning that in the vicinity of the substrate, the solution is depleted of Ni $^{2+}$. By stirring the solution, the solution is kept homogeneous in the whole volume. When preparing Ni metallizing solution the rate of stirring was 100/rpm. At this rate the homogeneity of solution was assured and it also helped to avoid solution decomposition.

3.3.  Sample Preparation for Electroless Co Deposition

Electroless Co deposition follows the same steps as electroless Ni deposition with respect to the surface cleaning, sensitization, catalyzing and immersion in electroless Co metallizing bath. The differences are given by the composition of the metallizing bath which can be found in Table 3.2-3 and by the pH (9.5) and the temperature used during
the deposition process. Another difference is given by the stirring of metallizing solution, for Co metallizing solution the stirring rate is 200/ rpm.

Table 3.3-1 A scheme for electroless deposition of Co.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion Time in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizer</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec.</td>
</tr>
<tr>
<td>Activator</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec</td>
</tr>
<tr>
<td>Co metallizing pH= 8.5 t= 55°C.</td>
<td>300 sec</td>
</tr>
</tbody>
</table>

3.4. Sample Preparation for Electroless Ni-Co-Co deposition

Electroless co-deposition of Ni-Co follows the same steps as electroless Ni deposition with respect to the surface cleaning, sensitization, catalyzing and immersion in electroless Ni-Co metallizing bath.

The differences are given by the composition of the metallizing bath which can be found in table 3.2-3 and also by the pH and the temperature using during the deposition process. Another difference is again related to the number of rotations/per minute-stirring while preparing the metallizing solution. For Ni-Co metallizing solution the stirring rate was 600/rpm. In addition in the composition of metallizing solution for Ni-Co-co deposition a new component was used: Rochelle salt. Rochelle salt is a complexing agent. Without a complexer, the metals precipitate out as hydroxides.
Table 3.4-1  A scheme for electroless co-deposition of Ni-Co

<table>
<thead>
<tr>
<th>Solution</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizer</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec.</td>
</tr>
<tr>
<td>Activator</td>
<td>60 sec</td>
</tr>
<tr>
<td>Rinsing</td>
<td>30 sec</td>
</tr>
<tr>
<td>Ni-Co metallizing Solution</td>
<td></td>
</tr>
<tr>
<td>pH = 9.5</td>
<td>300 sec</td>
</tr>
<tr>
<td>t = 83°C</td>
<td></td>
</tr>
</tbody>
</table>

An overview for electroless Ni-Co deposition

3.5. Reproducibility of the experiment:

For depositing Ni ultra thin films we repeated the experiment at pH 4.0 and 53°C and stirring rate 100 rpm, three times. Under these conditions we observed a very low deposition rate. We did not achieve continuity of the films. The deposition took place only on isolated islands. Using the same conditions regarding pH and temperature, we increased the stirring rate of solution at 200 rpm. The quality of films did not improve meaning that the deposition took place only in islands without perfect continuity. We repeated the experiment three times. At pH 4.4 and temperature of 53°C the quality of films improved (some islands merged), but without achieving the continuity of the films. At this pH we repeated the experiment 3 times. The stirring rate of the solution was 100 rpm. Under the same conditions regarding the pH and temperature, but at the stirring rate of 200 rpm, we repeated the experiment three times. We did not obtain better film quality. We deposited Ni thin films at pH 4.8 and 53°C three times. The quality of the films seemed much better: we achieved continuity of film, but the thickness was not satisfactory. That means that by the simple inspection of films with naked eye, when they
were exposed to light, they were partially transparent, we could see the light passing through. The stirring rate was 100 rpm. The experiment was repeated under the same conditions but at the stirring rate of 200 rpm, three times but the quality of films did not improve. At pH 5.2 and temperature 53°C and stirring rate 100 rpm, we repeated the experiment three times. The films seemed to have an improved quality, the continuity of films was achieved and the films were not optically transparent. Examining them with naked eye, we noticed that the light could not pass through. The same quality of films was achieved when we repeated the experiment for pH 5.3 and 53°C and stirring rate of 100 rpm. At this pH, temperature and stirring rate, the experiment was repeated three times. It was obvious that under the last conditions (pH=5.3, temperature 53°C and stirring rate 100 rpm), we obtained the best quality films (continuity was achieved and they were not optically transparent which means that a good thickness was achieved). In our case a good thickness is in the order of nanometers. The composition of the metallizing bath was kept constant.

For Co thin film deposition the experiment was repeated three times using pH=8.5 and 55°C temperature and the stirring rate of 200 rpm. At this pH we were able to deposit only some isolated islands. The film had no continuity. The experiment was repeated three times for pH 8.5, 55°C and 200 rpm. A continuous thin film with even thickness was obtained. At this pH and temperature the films were not transparent when examined in light with the naked eye. The composition of the metallizing bath was kept constant. At higher pH (10.5) and 75°C, the composition of the metallizing bath became turbid and no thin film was deposited. The experiment was repeated three times under these conditions three times.
For Co–Ni co deposition the experiment was repeated three times using 50% Ni and 50% Co, pH 10.5, temperature 83°C. The stirring rate for the metallizing solution was 600 rpm. The amount of Rochelle salt was 50 g. Under these conditions we were not able to deposit thin films. The metallizing solution was turbid and precipitation took place. For 70% Ni and 30% Co, pH 10.5, temperature 83°C, stirring rate 600 rpm, we were not more successful. Under these conditions films were deposited, but after the third trial the metallizing bath got contaminated and the film was deposited all over including the walls of the beaker. The amount of Rochelle salt used was 50 g. We tried three times more using the same percentage of Ni and Co, the same pH, and temperature and stirring rate, but using a different amount of Rochelle salt (100 g). The solution got contaminated after the second trial. The experiment was repeated under the same conditions with regard to pH, temperature, stirring rate, but with 200 g Rochelle salt. The same difficulties as before were encountered, decomposition of solution. At 30% Ni and 70% Co, pH 10.5, temperature 83°C, 600 rpm and using we could not deposit a film. Three trials were done using different amount of Rochelle salt: 50, 100, 200 g. The films could not be deposited under these conditions.

At 65% Ni and 35% Co, pH 9.5, temperature 83°C, stirring rate 600 rpm, the best quality films were obtained, meaning continuity of films was reached and the films were not transparent when exposed to light and examined with naked eye. The experiment was repeated three times using the same amount of Rochelle salt 200g.


3.6.1. Imaging Mechanism with Scanning Acoustic Microscopy
For imaging purpose two kinds of scanning acoustic microscope were used. The first one UH3 Olympus was used to inspect the surface, and interface of thin films system using a frequency of ultrasound of 600 MHz. The second acoustic microscope Leitz ELSAM was employed to study the subsurface and interface of thin films systems using a frequency of ultrasound of 1GHz. Increasing the frequency of ultrasound will lead to an increase in resolution of images.

![Diagram of Scanning Acoustic Microscope](image.png)

**Figure 3.6-1  The imaging mechanism of scanning acoustic microscope**
Summary of imaging principle using tone burst wave mode (Courtesy of Dr. Miyasaka)

Specifically, in Figure 3.6-1, the imaging mechanism of the SAM is described, in details. An electrical signal (i.e., tone-burst wave) is generated by a transmitter which sends the signal into a piezoelectric transducer (i.e., zinc oxide), located on the top of a buffer rod through a circulator that directs the electric signal. The role of transducer is to convert the electrical signal into an acoustic signal (i.e., ultrasonic plane wave). The ultrasonic plane wave travels through the buffer rod, made of sapphire, to the lens. The lens is located at the bottom of the buffer rod. The lens is coated by a layer called “acoustic anti-reflection coating” (AARC), made of silicon oxide. The role of this layer is to match the acoustic
impedance of lens and of the substrate. Without matching the acoustic impedance of the
two media (lens and substrate) the ultrasound cannot travel from the lens into the
substrate. The lens transforms the ultrasonic plane wave to an ultrasonic spherical wave
(i.e., ultrasonic beam).

The ultrasonic beam is focused within the specimen, and reflected back from the
specimen. The reflected ultrasonic beam, which carries the acoustic information about the
specimen, is again converted into an ultrasonic plane wave by the lens. The ultrasonic
plane wave returns to the transducer through the buffer rod. The ultrasonic plane wave is
again converted into an electric signal by the transducer. The electric signal comprises
transmission leaks internal reflections from the interface between the lens and the AARC,
and reflections from the specimen. Therefore, the reflections must be selected by a
rectangular wave from a double balanced mixer (hereinafter called simply “DMB”) which is known as the first gate. The gated electric signal has a peak of the amplitude
which is detected by a circuit, which includes a diode and a capacitor (i.e., the peak
detection technique). The gate noise is removed using the second gate which exists within
the first gate (the blanking technique). The peak-detected signal is stored into a memory.
This flow of processes allows the information that is collected at a single spot on the
specimen to be displayed as intensity at a certain point on the computer monitor.

In order to form a two-dimensional acoustic image, an acoustic lens and an X-Y
stage are mechanically scanned across a certain area of the specimen. The acoustic lens
can be moved axially along the z direction. Moving the lens on z axis will lead to a
variation in the distance between the specimen and the lens for sub-surface visualization.
For visualizing the surface of the specimen, the acoustic lens is focused on the specimen
(z = 0 μm), and for visualizing a subsurface of the specimen, the acoustic lens is mechanically defocused toward the specimen (z = - x μm, where x is the defocused distance).

It seems evident that the acoustic waves that give rise to the ‘picture’ are sensitive to the material structure differences, such as inclusions, amorphous and crystalline structure, cracks, voids, flaws, thickness variation, etc. In other words, rigorous correlation exists between the physical and chemical make up of materials and their structure and visco-elastic properties. Binding forces, in general, are nonlinear and cause nonlinear modulation of the reflected waves in the ultrasonic frequency range. As a result, the higher harmonics, which may be generated by the excitation of an interface as a result of a single frequency wave, allow information to be obtained about the properties and structure of the metal at the interface.
Chapter 4  Results

4.1.  Electroless deposited porous ultra thin Ni-Co films

Ultra thin Ni-Co films were deposited similar to electroless Ni ultra thin films. Since each metal is capable, independently, of electroless deposition it was possible to produce Ni-Co ultra thin films from alkaline baths. After deposition they were examined with optical and acoustical microscopes in order to detect the presence of pores. Using the exquisite sensitivity of SAM, it was possible to determine the presence of pores.

4.2.  Evaluating Ni-Co ultra thin film using the optical microscope

Evaluating ultra thin metal films using an optical microscope is a very difficult task since the thin metal films are opaque to the light. From the pictures below it seems, obviously, that regardless of magnification the defects and the pores are not visible.

When a green filter was used, some of the defects located at the surface were visible, but the defects located at the interface could not be visualized.
4.2.1 Optical Pictures

![Picture (a)](image1.png)  ![Picture (b)](image2.png)

**Figure 4.2-1** Specimen Ni-Co bad thin film.
The bar represents 200µm. The pictures were 20X magnified. Dimensions 250 x 187.5 mm
Figure 4.2-1 a represents an optical picture taken with reflection optical microscope. An ultra thin film (thickness 120nm) is opaque, and with conventional optical microscope the defects on the surface and interface of the thin films system are not visible.
Figure 4.2-1 b represents an optical picture taken with the same microscope but a green filter was added. Some of the defects situated at thin film surface were visible. The defects situated on interface were still not visible.
Figure 4.2-2 Specimen Ni-Co bad thin film
Figure 4.2-2 (a) represents an optical picture taken with reflection optical microscope. The bar represents 100μm. The pictures were 200X magnified. Dimensions 250 x 187.5 mm
Figure 4.2-2 (b) depicts an optical picture of the same specimen taken with reflection optical microscope, when a green filter was used. Some of the defects present at the surface were visible. The defects situated at the interface were not visible.
Figure 4.2-3  Specimen Ni-Co good thin film
Figure 4.2-3 a represents optical pictures taken with the same reflection optical microscope used for the other specimens of Ni-Co. The bar represents 200 μm and the pictures were taken with 4 X magnification. dimensions 250 x 187.5 mm
Figure 4.2-3 b for which a green filter was used shows some defects present at the surface of Ni-Co specimen. The defects are evidently much fewer than in the case of the other specimens
4.3. **Surface and Interior Evaluation of Ni, Co and Ni-Co Ultra Thin Film using Scanning Acoustic Microscope**

The ability to image below the surface of ultra thin metal films is an attractive property of the acoustic microscope. Ultra thin metal films are opaque to light but they are transparent to acoustic waves. Due to this ability, scanning acoustic microscopy provides valuable insights regarding ultra thin films structures and subsurface imaging which cannot be obtained any other way.

In order to form a surface acoustic image, the acoustic lens was mechanically scanned in X-Y directions across a certain area of thin films systems. For visualizing the surface of the ultra thin metal film, the acoustic lens was focused on the specimen. \( z = 0 \ \mu m \). For visualizing the sub-surface, interface the acoustic lens was mechanically defocused toward the film \( z = - x \ \mu m \). From the pictures below it seems evident that the acoustic waves are sensitive to the material structure differences, such as inclusions, amorphous and crystalline structure, cracks, pores, flaws, thickness and variation.

4.4. **Contrast Mechanism in the Scanning Acoustic Microscope-The V(z) effect**

In traditional microscopy resolution is of a great interest. However, the significance of the scanning microscope does not rest in its resolution alone. For instance image contrast is of a stronger interest. Image contrast observed in acoustic microscopy can be related to the elastic properties at the surface as well as below the surface of the sample.

The image contrast observed in acoustical pictures is related to elastic properties near the surface as well as below the surface of the sample and interface of the sample. Thus, acoustical images are not comparable with optical images.
The interpretation of the contrast is a major task and of essential interest.

When the acoustic lens is focused at the surface of the specimen, only specular reflection is generated, and the acoustic contrast is very weak. When, however, the lens is focused below the surface the contrast becomes much stronger. Especially in defocusing scanning, a series of oscillations in the transducer output is observed. This effect is known as the acoustic material signature or, simply, the V(z) curve, and it is a function of the defocus z. V(z) is an interference result between the nonspecularly reflected surface acoustic waves excited in the specimen and specularly reflected waves.
4.4.1 Acoustical pictures

(a) Z=0µm
(b) Z=-3.5µm
(c) Z=-5.5µm

50µm

Figure 4.4-1 Specimen: Ni
Specimen: Ni at pH=5.3; T=55°C. Frequency: 600MHz. Scanning Width: 250 x 187.5 mm
In fig. 4.4-1 a. the focal point is on the film surface (z=0 µm). In image 4.4-1 b the focal point is lowered at 3.5 µm (z=-3.5µm) while image 4.4-1 c corresponds to focal lowering by 5.5µm (z=-5.5µm). The z values are indicated under each picture. The bar represents 50µm.
Figure 4.4-2 Specimen Co
Specimen: Co at pH=8.5; T=55°C Frequency: 600MHz. Scanning Width: 250 x 187.5 mm
Figures 4.4-2a the focal point is on the film surface (z=0 µm). Figures 4.4-2 b the focal point is lowered at 4.0 µm (z=-4.0µm) and finally figure 4.4-2 c depicts the SAM image where focal point is lowered at 8.5 µm (z=-8.5µm) Here too the z values are indicated under each picture. The bar represents 50µm.
Figure 4.4-3 Specimen Ni-Co
Specimen Ni-Co at pH=10.5; T=83°C. Frequency: 600MHz. Scanning Width: 250 x 187.5 mm
Figures 4.4-3a represents an acoustical pictures with the lens focused on the films surface (z=0 µm). Figure 4.4-3b the focal point is lowered at3.5 µm (z=-3.5 µm). The many dark spots evident are probably the pores of the film. The pores do not reach all the way through the film as can be seen in the figure 4.4-3 c where the focal point is lowered at 5.5µm (z=-5.5 µm). The bar represents 50µm.
Figure 4.4-4  A comparison between optical picture and acoustical picture
Figure 4.4-4 a represents an optical image obtained by a reflection light microscope (Leica) with 200 X magnification. The image shows the surface of the thin film system including defects at the interface. Since an ultra thin film (thickness 120nm) is opaque, conventional optical techniques cannot detect a defect located at an interface between the thin films an substrate. Figure 4.4.-4 b shows an acoustic image formed with frequency of ultrasound at 1.0 GHz, and shows the existence of micro-cracks, delaminations and the like. The acoustic lens was focused onto the surface of the specimen (z= 0 μm).
Figure 4.4-5  Acoustic images formed with frequency of ultrasound at 1.0GHz
Figure 4.4-5 a shows an acoustic image, where the acoustic lens was defocused onto the surface of the specimen (i.e., $Z=-5\mu m$) and shows the existence of micro-cracks, delaminations and the like. The image shows the interface of the thin film system including defects at the interface. Figures 4.4-5 b, 4.4-5 c, depict the SAM images obtained when the lens were further defocused (i.e., $Z=-10\mu m$, respectively $Z=-15\mu m$) toward substrate. It is evident that defocusing the lens the contrast of the pictures will increase allowing detections of minute details. Here too the $z$ values are indicated under each picture.
Chapter 5  Discussion

A method that can be useful for further improvement of designing and manufacturing ultra thin metal films was developed in this research. The developed method is a combination of two techniques: a classic one for the deposition of ultra thin metal films (i.e., electroless deposition) and a complementary NDE technique for quality evaluation of the films. Using the advantages of electroless deposition over the other deposition methods, porous nickel cobalt ultra thin films were obtained, which might be used as coatings for orthopedic implants. Among the requirements that ultra thin metal films for coatings implants should meet, good adhesion is very important, affecting the performance of an ultra thin metal film in medical applications.

Therefore, this study also focused on the investigation of a nondestructive method (i.e., scanning acoustic microscopy (SAM) to evaluate the quality of nickel cobalt ultra thin films grown on a dielectric substrate

5.1.  Ultra Thin Metal Films Obtained by Means of Electroless Deposition

5.1.1.  Electroless Deposited Ultra Thin Metal Films

Using electroless deposition a porous nickel cobalt thin film was obtained. This type of film might be used as coating for biomedical implants. It was shown that the use of porous metal coating over an implant lead to a decrees of stress shielding and thus to a decrease in bone resorption (Pilliar, 2004; Perla et al., 2005). The other qualities of porous metal coatings deposited on implants and the techniques for their deposition were already mentioned in chapter 1, section 1.1.2 and 1.2. However, all these deposition methods have some disadvantages such as high temperature, uneven coatings, useless and hazardous byproducts, low corrosion resistance
not very good adhesion of the ultra thin film to the substrate and hence low biocompatibility (Ziegler, 1992; Pilliar, 2004; Huang, 2005).

The ultra thin Ni, Co and Ni-Co films obtained by electroless deposition are not only porous, but also amorphous. The amorphous character of these films is due to the presence of P in all film. Consequently, the ultra thin films are not pure Ni, Co or Ni-Co. The obtained ultra thin films are Ni-P, Co-P and Ni-Co-P. The presence of phosphorus is due to the reducing agent used in the deposition process (sodium hypophosphite). If instead of sodium hypophosphite other reducing agents would have been used such as reducing agents containing boron, boron would be present in the final product. Some researchers claimed that the presence of phosphorus is more advantageous than presence of boron. It seem that the presence of phosphorus in the thin films confer them a better corrosion resistance (Mallory et al., 1990; Krishnan et al., 2006).

As shown in section 1.3, using the advantages of this technique, it was tried to overcome some of the problems raised by the other methods used for depositing coating for biomedical implants. Other important characteristics are maintaining a good elastic modulus of implant.

It was hypothesized that due to the reduced thickness of thin films (about 100nm), the pores present were even smaller than 100nm since the thickness of thin film is about 100nm. If this hypothesis is correct, it would mean that the absorption of bone protein into implant is even better than it was previously obtained with other nano phase coatings (Webster et al., 2000).

5.1.2. Activation and Sensitization of Dielectric Substrate
In order to deposit nickel (Ni), cobalt (Co) and nickel-cobalt (Ni-Co) ultra thin film, it was used a sensitization bath containing SnCl₂ and hydrochloric acid and a catalysis bath formed from PdCl₂ and hydrochloric acid.

For deposition of ultra thin Ni, Co and Ni-Co films it was preferred the two steps activation process. The reason was that in one step activation process various Sn-Pd chloride instable complexes may form (see section 1.3.2). Moreover, in one step activation process is more difficult to expose Pd particles adsorbed on the dielectric substrate (see section 1.3.2) which makes the whole process of deposition less efficient.

Palladium is needed at the substrate surface in order to reduce the metallic ions: Ni, Co or Ni-Co. The higher the palladium surface concentration, the higher the deposition rate is. This can be explained by the reaction that takes place at the palladium surface.

![Diagram](image-url)

**Figure 5.1-1 Reactions at the palladium interface**

Palladium plays a major role at the beginning electroless deposition process. Hydrogen is absorbed onto palladium in an ionic form, leading to the formation of active of active palladium in a metallic form (Touyeras et al., 2005).

At the palladium surface the adsorption reaction decreases the presence of hydrogen in solution, and therefore decreases the competition between the reduction of
metal and the reduction of hydrogen. This would lead to an increase in the plating rate at the beginning of the electroless deposition process.

Proper activation of the substrate to be plated is very important for quality results. Poor surface preparation can cause lack of adhesion, roughness, non-uniform coating and/or dark deposits (Mallory et al., 1990). However, in the present investigation the substrate used was glass, precleaned prior deposition process. Even though the substrate was precleaned in some occasions it probably contaminate with impurities and obtained of the deposited films had a poor adhesion and/or blistering. Usually with electroless deposition the deposits are even and smooth, but when the substrate is not properly cleaned the deposited films may be rough. In order to avoid deposition of thin films with defects the substrate was cleaned with distilled water, between the steps of deposition process.

5.1.3. The reason for using a dielectric substrate

Investigation in the field of electrophysiology shows that bioelectric phenomena of different origin are present in bone, the most important being the bioelectric potential connected with bone viability and metabolism. Dobrev and Vladimirov have shown that the negative biopotential is high at the fracture site where metabolism is also increased. During healing the negative values decrease and when it is complete the configuration of biopotentials along the length of the bone regains the pattern characteristic of intact bone. Moreover, it has been noticed that a more stable osteosynthesis is achieved when using dielectric implants (Dobrev et al., 1984; Brovarone et al., 2006). For instance if metal devices are used for osteosynthesis to obtain stable fixation of the fragments, they may produced a “short-circuit” of biopotentials along their length, so depriving the bone of
necessary negative biopotential. Consequently the intensity of the metabolic processes is also reduced, leading to a relative delay in callus formation (delay in bone osteosynthesis and consequently healing).

Therefore, when a dielectric device is used there is no flattening or reduction of the required negative bioelectric peak at the fracture site. This device produces no ill-effects on the normal longitudinal distribution of bioelectric potential in the damaged bone and consequently does not interfere with the normal healing processes, but still produces a stable osteosynthesis. Hence the period of callus formation is shortened, in other words the period of post operative bone in growth is shorter (Ducheyne et al., 1992).

Moreover, due to the fact that dielectric implants mimic as well as possible the dielectric bone structure (Fois et al., 1999), the use of glass as a model substrate seams meaningful.

The substrate (glass) was preacleaned, because in electroless deposition process, this cleaning step is very important for achieving an ultra thin film with enhanced corrosion resistance (Agarwala et al., 2006).

5.1.4. The use of Ni

It has been shown that electroless Ni ultra thin films exhibits a good corrosion resistance (Agarwala et al., 2006; Krishnan et al., 2006). Good corrosion resistance is a very important characteristic to be achieved in both industrial and medical applications.

However, in medical applications corrosion resistance is not the only concern. Biocompatibility is also a very important feature if ultra thin metal films are used as coating for medical implants.
For instance, there are studies showing that porous Ni-P coatings can be utilized not only to provide corrosion resistance to the surfaces of medical implants, but also due to their biocompatibility, porosity and amorphous structure, can be utilized to deliver drugs in the human body (Gertner et al., 2003).

Es-Souni and Armitage have shown that various studies have been conducted to assess the biocompatibilities of nitinol (NiTi), which has been increasingly used in the last two decades in medical applications (Armitage et al., 2003; Es-Souni et al., 2005). They reported in their review regarding the biocompatibility of nickel titanium shape memory alloys, that the majority of research testifies to a good biocompatibility both in vitro and in vivo.

In addition, porous Ni-Ti fusion devices were found to be with higher corrosion resistance than their counterparts' nonporous devices (Schrooten et al., 2007).

However, there are some studies that attribute poorer compatibility to nickel (Bass et al., 1993; Assad et al., 2002). It was shown that the reason that leads to a poor biocompatibility of nitinol is the corrosion product of nickel (Es-Souni et al., 2005).

However, porous electroless deposited Ni-P thin films may provide a very good corrosion resistance to the surfaces onto which they are deposited, since they are amorphous. Amorphous structure is useful for medical purposes, due to the fact that amorphous structure exhibits higher corrosion resistance (no grain boundaries).

5.1.5. The use of Co

It is well known that cobalt has a good biocompatibility (Aionicesei et al., 2006). On the other hand it has been shown that Co-P alloy has grain boundaries and consequently less corrosion resistance than Ni (O'Sullivan et al., 1998).
5.1.6. The use of Ni-Co

Therefore, in order to get an ultra thin metal film which might provide both corrosion resistance and biocompatibility, a nickel-cobalt ultra thin film was obtained using electroless deposition. It is possible to deposit nickel-cobalt-phosphorus alloys with a complete range of nickel-cobalt compositions from alkaline bath, since each metal is capable, independently of electroless deposition.

It has been shown that different studies were carried out to test the corrosion resistance of Ni-Co alloy. The experimental alloys made of mixtures of Ni-Co powders shown encouraging properties regarding corrosion resistance (Hejwowski, 2006). Narayanan et al carried studies regarding the microstructure of Ni-Co-P thin films showing that these types of films have higher corrosion resistance than Ni-P or Co-P (Sankara Narayan et al., 2003).

In addition, it has been shown, that amorphous structure of Ni-Co-P alloy provides higher corrosion resistance than non amorphous ones. In electroless deposition process, the extent of segregation of metalloid alloy (phosphorus or boron) in the coating determines its crystalline structure. Since the required amount of phosphorus segregation (8.1–9.0 wt.% for samples with different metallic ratio of Ni^{2+}/Co^{2+}) is relatively large, nucleation of nickel cobalt phase is prevented, and this has resulted in amorphous structure (Sankara Narayan et al., 2003).

Since in the present investigation the concentration of phosphorus in Ni-Co-P alloy was in the range of 5.5-6.9% (Schlesinger et al., 2000), the microstructure of obtained porous nickel-cobalt -phosphorus film was amorphous providing a better corrosion resistance. Moreover, due to the fact Ni is combined with biocompatible Co the film might provide a good biocompatibility.
5.2. Problems with Electroless Deposition of Ni-Co-P thin films

5.2.1. Decomposition of metallizing solution

One of the problems encountered during deposition of Ni-Co was the effect of plate-out or decomposition of the metallizing bath. This is probably related with the formation of phosphates and precipitation of Ni phosphate and Co phosphite (Mallory et al., 1990; Agarwala et al., 2006). Since there is a co-deposition the amount of phosphite will increase faster than in case of Ni or Co deposition. In this case the metallizing solution will become cloudy and give poor adhesion. In the present research, a way to prevent contamination with phosphate was to increase the pH and to improve the stirring of the solution (600/rpm).

The plating rate was found to increase with increase in pH from 8-10 for Co and Ni-Co, beyond which the bath becomes destabilized. At pH around 11 bath will begin to decompose. Hence, is safer to use a bath approximately pH 9.0, where there is a good plating rate as well as a good stability of the bath (Sankara Narayan et al., 2003).

In spite of all of these problems, all related with the tight control of the metallizing bath, electroless deposition seems to be a better technique to deposit metal thin films with improved qualities for coating medical implants.

5.2.2. Contamination of the Solution

When all other parameters appear to be in order, extraneous contamination of the solution may appear.
Palladium is used in the activation of non-catalytic substrate in this case for activation of a dielectric substrate glass. If not rinsed properly, palladium ions or particles may be introduced into the electroless bath, which will form nuclei and cause spontaneous decomposition of the plating bath. Thus, between steps of deposition, rinsing with distilled water played a very important role.

In addition the quality of deposited films depends very much on agitation (stirring). A poor agitation will lead to pitting of the thin film (Mallory et al., 1990)

Dark deposits may appear if after the EN plating, the deposit is rinsed with contaminated water. Therefore when preparing Ni-Co ultra thin films, the stirring rate was increased to 600 rpm (compared with 100rpm for Ni and 200rpm for Co), to prevent contamination of the solution.

5.2.3. Plating Rate

The plating rate is found to increase with an increase in pH from 8.0 to 10.0, beyond which, the bath becomes destabilized and at approximately pH 11.0, decomposition of the bath occurs (Agarwala et al., 2006; Krishnan et al., 2006). Hence, it was safer to use the bath at approximately pH 9.0, where there is a good plating rate as well as stability of the bath.

5.2.4. The Effect of Temperature:

The temperature at which the plating reaction occurs is the principle variable that determines the rate of reaction (Mallory et al., 1990). If the temperature is allowed to increase much beyond 90°C, the possibility of solution plate-out or even solution
decomposition increases. Consequently, working temperature was 85°C to avoid the risk of plating-out and decomposition of metallizing solution.

5.2.5. The influence of H⁺

It was observed that for every mole of Ni²⁺ deposited, three moles of H⁺ are generated (Mallory et al., 1990). Consequently the accumulation of hydrogen ions in the plating bath lowers the pH of the solution. It was observed during experiments that the most noticeable change in the plating process was a decrease in the plating rate. The observations were in agreement with other experiments (Krishnan et al., 2006). It was also noticed that when the pH was dropped below 4.0 (pH< 4.0), no deposition took place.

5.3. Evaluation of Ultra Thin Metal Film using High Resolution Acoustic Microscopy

To assure adequate quality of ultra thin metal deposits we illustrate the use of high frequency mechanical scanning acoustic reflection microscopy. Specifically, high resolution acoustical imaging provides the opportunity to determine and visualize defects in ultra thin metal film as well on the interface metal-substrate. Especially working at operative frequencies of 600 MHz and 1GHz is a very attractive opportunity, because at these frequencies it can compete with the optical microscope in resolving fine details. In addition, working with the scanning acoustic microscope helped to overcome the problem of the optical microscope when used for examining opaque materials. The optical microscope cannot be used to examine opaque materials such as ultra thin metal films. For acoustic waves, opaque materials are transparent. But there is a stronger objection to the optical microscope, which can be extended as well to the scanning electron
microscope, that they cannot be used to examine mechanical and elastic properties of ultra thin films microstructure. These elastic properties are fundamental—they make a difference as to whether the structures will hold together. The ability to examine these properties on a microscopic scale allowed us to detect all the features present in ultra thin film systems (such as: porosity, micro cracks, and delaminations).

Scanning acoustic microscopy has a number of advantages: it is a non-destructive method and one which does not require special preparation of the sample surface, it allow the determination of not only important quantitative material parameters such as the elastic modulus and mechanical energy loss, but also qualitative material characteristics.

The advantages inherent to scanning systems with focusing were not obvious in the beginning. It is now becoming evident that scanning systems which record a single point at a time exhibit properties different from those that display the entire field of view. In the scanned system there is no problem with coherent radiation. Since the energy at the focus is confined to a diameter that is less than one wavelength in dimension there are no interference fringes of the type that are common with optical microscopes (Quate et al., 1979).

5.3.1. Contrast Mechanism in the Scanning Acoustic Microscope—The V (z) Effect

The significance of the scanning acoustic microscope does not lie in its resolution alone. Image contrast is even more important. Image contrast observed in acoustic microscopy is related to the elastic properties at the surface as well as below the surface (Yu et al., 1995). This feature makes acoustic microscopy so important in evaluation of metal ultra thin films since this feature is not shared with any other kind of microscopy. Fringes that are seen in acoustical pictures are an interference effect associated with
waves that can be excited in the surface of specimen. It is not simple problem to interpret the contrast of these fringes. It cannot be said that a brighter area corresponds to a higher (or lower) density, or to a greater (or smaller) elastic modulus. In addition, the contrast varies very sensitively with focusing, defocusing of lens, in other words with the distance between the lens and the surface of the specimen. This behaviour is best visualized as V (z) curve. The V (z) curve is the “source of contrast” and it is used to record quantitative and qualitative information on the elastic properties of a specimen with microscopic precision (Yu et al., 1995; Parthasarathi et al., 1997).

Acoustic microscopy is emerging to be a powerful tool for both qualitative and quantitative non-destructive characterization of a wide range of materials. Quantitative acoustic microscopy primarily involves the measurement of the received acoustic amplitude as a function of the distance (defocus) between the lens and the sample. This response, characterized by a series of nulls and maxima, is often referred to as the acoustic material signature (AMS) or V (z) response (Briggs, 1992).

The V (z) response is caused by the generation and propagation of surface acoustic wave at the liquid-solid interface. The lens creates a cone of longitudinal waves which propagate through the water and strike the water-sample interface at various angles. The Rayleigh critical angle for the water sample media is the angle at which an incident longitudinal wave is converted into a Rayleigh wave (which propagates along the liquid-solid interface). If the cone of longitudinal waves includes the Rayleigh critical angle (implies that the semi-numerical aperture angle of the lens is greater than the Rayleigh critical angle \( \theta_R \)), then a leaky Rayleigh wave is generated. Longitudinal waves meeting the solid surface at the Rayleigh angle result in the generation and propagation of
leaky Rayleigh waves at the liquid-solid interface. The Rayleigh wave is called leaky because it radiates or 'leaks' energy into the fluid as it propagates on the surface of the solid. Another name of leaky Rayleigh wave is surface acoustic wave (SAW) wave (Parthasarathi et al., 1997).

SAW is a very important parameter for images obtained in the tone burst wave mode. In tone burst wave mode lenses have aperture angles of 120. The contrast in the images formed by acoustic lens that have the aperture angle of 120 changes in the accordance with the position of the focal point controlled by the movement of the acoustic lens along $Z$ axis. This contrast mechanism is explained by the change of the receiving voltage in the transducer associated with the excitation of the SAW. When the aperture angle of the acoustic lens is large, surface acoustic wave are generated because the incident angle goes beyond the Rayleigh critical angle.

Another factor that causes the appearance of contrast in the acoustic picture is reflectance function. Reflectance function affects the $V(z)$, which depends on the elastic properties of the material. When a specimen includes an elastic discontinuities, such as an edge, a step, a crack or a joint interface, an acoustic image of the elastically discontinuous and peripheral portions visualize by the scanning acoustic microscope shows unique contrast, for example, fringes or black stripes (Yu et al., 1995; Miyasaka et al., 2002).

5.3.2. Types of Defects in Electroless Deposited Ultra Thin Films

The images shown in Figures 4.4-1, 4.4-2 to 4.4-5 have not been analyzed in any detail. The main aim in this research was to investigate if SAM is a good method for quality evaluation of ultra thin metal films and to illustrate the usefulness of SAM methodology in analyzing electrochemically deposited films. Once again it is important
to stress that samples to be analyzed do not require any special preparatory pre-treatment, in addition to the fact that they do not require to be in vacuum as, for instance, in case of most high resolution microscopic methods. Moreover, for the sake of clarity in case of our representative samples, it should be noted that those were grown outside a clean room and so the number of defects is rather copious and easily evident.

Despite the above, we note that as the 'z' value changes and the image moves deeper into the sample the contrast and with it the details of the image (compare plates a to b) in Figure 4.4-3, for instance change markedly. The many dark spots evident on Figure 4.4-3 b, maybe due to thin metal film porosity. This is possible due to the exquisite sensitivity of the acoustic microscope to the small details as porosity (Parthasarathi et al., 1997). The pores do not reach all the way to the substrate as seen in plate c of the figure. Compare this to the images in Figure 4.4-2. Here actually the pores appear, in about equal intensity, on all three plates indicating the survival of the holes all the way through the film. With regard to Figure 4.4-1 two qualitative points may be made. The one is that the defect in the middle of the plates shows its rims not properly adhering to the substrate. This is evident in plates b and c but much less so on the surface only image i.e. plate a. Second, in that vain, it is only in plates b and c that a pale area in the lower right corner is evident. Again poorer adhesion seems to be the culprit which may manifest itself on the images as areas of different contrasts.

The lateral and vertical resolutions are estimated to be about 1.75μm and 2.5μm respectively. Those are calculated using the formula as follows:

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\[ \Delta r = F \lambda = F \left( \frac{v_w}{f} \right) \]

Equation 1

\[ \Delta \rho = 2F^2 \lambda \]

Equation 2

where \( F \) is a constant (in our system \( F \) is 0.7) related to lens geometry, \( \lambda \) is the wavelength in the coupling medium (i.e., water which in our system was about 2.5 \( \mu \)m), \( f \) is the frequency of the wave generated by the transducer (600 MHz in our system), \( v_w \) (about 1500 m/s) is the longitudinal wave velocity in the coupling medium.

Comparing to the thickness of the film, the vertical resolution calculated with longitudinal wave is too large to observe defects at the interface. Since the aperture angle of the lens is large (i.e., 120\(^\circ\)), we propose that one defocus the acoustic lens toward the substrate to generate a surface acoustic wave (SAW) when observing the adhesive problem at the interface (Quate et al., 1979; Liang et al., 1985; Wemple et al., 1978; Maeva et al., in press). The wavelength of the SAW is substantially less than half of that of the longitudinal wave. Furthermore, the SAW is very sensitive to discontinuities, and enhances the contrast. Therefore, we have an opportunity to see the adhesive problem at the interface.
Chapter 6  Conclusions and Recommendations

One of the objectives was to determine if a porous ultra thin nickel-cobalt film could be obtained by electroless deposition method. Porosity is an important and positive feature for medical applications of the ultra thin films. Through our laboratory experiments ultra thin nickel-cobalt films were obtained by the electroless deposition method and the presence of pores on their surface was verified using a nondestructive method (i.e., scanning acoustic microscopy).

Through the experiments it was proved that SAM is a good method for ultra thin film evaluation. A method was developed combining two techniques: electroless plating for ultra thin films deposition and a non destructive one (SAM) for quality evaluation of ultra thin metal films.

This work has important implication for further improvement of designing and manufacturing of the films.

The porosity, adhesion, micro-cracks, and delaminations included within ultra thin film systems have been successfully visualized and the quality of ultra thin nickel-cobalt films has been evaluated using a scanning acoustic microscope with a 120 aperture angle of the lens.

Moreover using the sensitivity of the scanning acoustic microscope when operated at high frequencies (such as 600 MHz and 1 GHz) not only porosity was detected, but the presence of micro-cracks and delaminations in the ultra thin nickel-cobalt films electroless deposited on dielectric substrate was noticed as well.

It is recommend that future research work to be focused on:

- measuring the dimensions of the pores on the ultra thin film surface

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- determining the ratio of pore surface/film surface
- investigating if nickel-cobalt ultra thin film poses any toxicity risks to humans
- testing *in vivo* utilization of ultra thin nickel-cobalt films
- developing a new non-destructive technique to investigate the *in vivo* utilization of ultra thin nickel-cobalt films
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