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## Growth study of nanoscale Re–Ni coatings on functionalized SiO<sub>2</sub> using electroless plating



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#### ABSTRACT

In spite of the unique combination of properties of Re-based alloys and the use of electroless plating in many relevant industries, the early stages of electroless plating of Re-based thin films have not been reported before. This paper is focused on the study of the early stages of growth of ultrathin (<20 nm) Re–Ni films with high Re-content by electroless plating on a functionalized-SiO<sub>2</sub> substrate. Each step, from the modification of the substrate to the formation of a continuous film, is characterized. Moreover, the effect of the addition of Ni<sup>2+</sup> ions to the bath is analyzed. The addition of a low concentration of Ni<sup>2+</sup> ions to the electrolyte is found necessary to obtain full surface coverage and thicker deposits. The as-deposited Re–Ni films consist of both amorphous Ni–Re and H<sub>0.57</sub>ReO<sub>3</sub> phases. The Re-content is not uniform along the thickness of the deposit, and has a maximal value at the percolation point. The deposition process is found to consist of sequential reduction reactions, from ReO<sub>4</sub><sup>-</sup> to lower valence oxides, to metallic Re.

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#### 1. Introduction

Rhenium (Re) is a refractory metal with a unique combination of properties. It has a high melting point ( $\sim$ 3170 °C), and excellent wear properties. However, unlike other refractory metals, pure Re does not form carbides, does not have a ductile to brittle transition [1] and has a hexagonal close-packed (HCP) crystal structure. Moreover, Re has the greatest tensile strength, excellent creep resistance over a wide range of temperatures (up to ~2000 °C), and a high modulus of elasticity [1–3]. For these reasons, Re and its alloys have attracted much interest in many industrial applications, such as: aerospace, nuclear, electrical, chemical, and biomedical [2–4].

The high cost of Re limits its use to special applications, such as Re-based alloy coatings and as an important catalyst in the petrochemical industry. Moreover, it is a useful alloying element for other metals, since it improves their mechanical properties in high-temperature applications [1–5]. Formation of Re-based alloy coatings by chemical vapor deposition (CVD) and electroplating

http://dx.doi.org/10.1016/j.apsusc.2014.05.178 0169-4332/© 2014 Elsevier B.V. All rights reserved. has been reported [2-4,6-10]. In our previous study, Re–Ni alloys with high Re-content (>75 at.%) were obtained by electroless plating onto Cu and SiO<sub>2</sub> substrates [11]. Electroless plating has the unique feature of selective deposition and formation of very thin layers on both conductive and non-conductive surfaces, without using an external power source or vacuum technology. Thus, electroless deposition of thin films was found to be a very attractive method for metallization in various micro- and nano-technology applications [12].

Thin films have been studied extensively in recent years due to their potential applications in nanotechnology. Different nickel electroless plated nano-coatings were proposed and studied [13–15]. In the current study we show the ability to form high quality and high Re-content, ultrathin Re–Ni coatings (<20 nm) on SiO<sub>2</sub> substrate using electroless plating. The same bath composition that was used for Re–Ni alloy deposition using dimethylamineborane (DMAB) as the reducing agent in our previous study [11] is employed in the current work. The SiO<sub>2</sub> surface is modified by aminopropyltrimethoxysilane (APTMS) before activation with Pdcitrate. The modification of the SiO<sub>2</sub> substrate by amino-terminated siloxane group is a well known process for improving the adhesion of the deposits to the non-conducting SiO<sub>2</sub> substrate. Moreover, the amino-terminated silane can be used for pattern formation on the SiO<sub>2</sub> surface by using UV irradiation [16].

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It was shown in our previous study that, when only perrhenate ions are used in the electrolyte, the deposition rate extrapolates to zero. However, even a very small amount of Ni<sup>2+</sup> ions added to the bath is sufficient to initiate the reaction, and Re–Ni films with high Re-content are formed [11]. Other studies of electroless plating that deal with induced codeposition of Re with Ni or Co, resulting in formation of Ni–Re [15] or Co–Re [17] alloys with low Re-content, have also been reported. Yet, the formation of pure rhenium coatings from a standard electroless plating bath has not been reported, when only perrhenate ions were used.

One of the key issues in producing high-quality ultrathin coatings is the behavior of the material during the initial stages of deposition. Yet, to the best of our knowledge, it was not investigated for electroless plating of Re-based alloys, and the mechanism of deposition has not been studied in detail.

In the current work, the early stages of Re–Ni film growth, during electroless deposition on a functionalized-SiO<sub>2</sub> substrate, are studied using high-resolution transmission electron microscopy (HR-TEM) and X-ray Photoelectron Spectroscopy (XPS). The influence of addition of Ni<sup>2+</sup> ions to the electrolyte on the film growth is studied by comparing films that are formed with or without Ni<sup>2+</sup> ions in the bath. Moreover, the electrical properties of as deposited Re–Ni films as a function of film thickness are evaluated. It is important to study electrical properties of the grown films because they are influenced by the composition, microstructure and thickness of the deposited layers.

#### 2. Experimental

Re–Ni films were formed by electroless deposition on  $SiO_2$  (100 nm)/Si substrates. The sizes of all samples were  $20 \times 20$  mm. All experiments were performed in a 25 mL open beaker containing 10 mL solution (freshly prepared for each experiment), without agitation.

First, all substrates were cleaned by RCA-I solutions [11], in order to remove all organic contamination. Afterwards, the substrates were rinsed in deionized water. The SiO<sub>2</sub> (100 nm)/Si substrate was modified by amino-terminated siloxane, in order to improve the adhesion of the Re–Ni deposits to the non-conducting SiO<sub>2</sub> substrate. In the next step, substrates were immersed for 3.5 h at 60–65 °C in a 1% solution of APTMS (terminated with NH<sub>2</sub> groups) in ethanol, to form a monolayer of silane on the surface. Subsequently, the samples were rinsed in ethanol using ultrasonic agitation. After silanization, the substrates were activated by dipping into a Pdcitrate solution for 20 min. Electroless plating bath with DMAB as the reducing agent was used for Re–Ni deposition. The composition of the solution and the operating conditions are shown in Table 1. The film adhesion was evaluated by the conventional "scotch tape" method. All samples passed this test.

TEM analysis was done in JEOL 2010F microscope equipped with STEM high-angle annular dark-field (STEM-HAADF) detector. TEM samples were prepared by a focused ion beam (FIB) FEI Helios NanoLab<sup>TM</sup> system using a protective SiO<sub>2</sub> cap layer. The morphology of the films during its growth, as well as the surface coverage, were characterized by high-resolution scanning

#### Table 1

Bath chemistry and operating conditions for electroless deposition of Re–Ni (Bath II) and Re (Bath I) films.

Bath chemistry and operating conditions	Bath I (mM)	Bath II (mM)
NiSO <sub>4</sub> .6H <sub>2</sub> O	0	3.45
KReO <sub>4</sub>	34.5	34.5
$Na_3C_6H_5O_7\cdot 2H_2O$	170	170
DMAB	100	100
pH	9.0-9.5	
Temperature (°C)	90-95	

electron microscopy (HR-SEM), using an FEI Helios NanoLab<sup>TM</sup> equipped with a sub-nanometer field emission gun. Images were taken with a 5 keV beam and a secondary electrons (SE) detector. SEM micrographs were analyzed using Image] software (NIH), to extract morphological kinetic parameters, such as surface coverage and island size distribution. The chemical states of the surface after every processing step were determined by means of XPS measurements performed in UHV ( $2.5 \times 10^{-10}$  Torr base pressure), using 5600 Multi-Technique System (PHI Inc., USA). High-resolution XPS spectra (HR-XPS) were taken at a pass energy of 11.75 eV, at increments of 0.05 eV. Curve fitting was done with Gaussian-Lorentzian function, using a 5600 Multi-Technique System software. The binding energy of adventitious carbon at 285 eV was taken as an energy reference for all measured peaks. An inline four-point probe (Lucas/Signatone<sup>TM</sup>) was used to measure the thickness dependence of films sheet resistance (Rs). X-ray diffraction (XRD) measurements were performed in a TTRAX III (Rigaku, Japan) diffractometer, equipped with a scintillation detector and a rotating Cu anode, at 50 kV and 240 mA. Using parallel beam optics formed by a multilayered mirror (Rigaku, Cross Beam Optics attachment), asymmetric  $2\theta$  scans with a fixed small incident angle (3°) were carried out. Qualitative phase analysis was made using MDI Jade 7 software (Materials Data, Inc., Livermore, CA).

#### 3. Results and discussion

### 3.1. Substrate pretreatment – silanization and activation procedures

In order to deposit on an insulator substrate, such as  $SiO_2$ , special pretreatment of the surface is needed. In our study, clean  $SiO_2/Si$  substrate is covered with APTMS self-assembled monolayer (SAM). The silanization process is employed using wet-chemical method before the activation procedure, in order to improve the adhesion of the coating to the substrate. This is a very important step, particularly in the case of nano coatings, since any variation during preparation, such as humidity, temperature and contamination, will result in formation of non-uniform thickness and poor adhesion.

In order to analyze the formation of the Pd-catalyst on the APTMS, the SiO<sub>2</sub>/Si surface was studied by XPS and TEM. Table 2 shows the SiO<sub>2</sub>/Si surface composition that was determined by XPS after modification by APTMS, and the following Pd-citrate activation. Nitrogen (N 1s) content of  $\sim$ 2 at.% confirms the presents of amine group on the surface after the silanization treatment. Following activation, Pd is also observed, see Table 2.

In order to quantitatively determine the oxidation state of the amino groups before and after Pd-activation, the HR-XPS N 1s spectrum was measured (Fig. 1). All measurements were done at a shallow take-off angle of  $25^{\circ}$ , for increasing surface sensitivity. The N 1s structure in Fig. 1a exhibits two peaks at 399.7 and 401.5 eV, corresponding to the unprotonated (NH<sub>2</sub>) and protonated (NH<sub>3</sub><sup>+</sup>) amine groups, respectively. The curve fitting of the N 1s structure before Pd-activation (not presented here) shows that the concentrations

#### Table 2

Surface composition (at.%) of the SiO<sub>2</sub>/Si substrate after different treatments.

Element	Modification with APTMS	Modification with APTMS followed by Pd-citrate activation	Electroless plating of Re on modified and Pd-activated surface
С	33.9	35	20.6
0	38.9	37.55	50
Si	25	25	24.9
Ν	2.2	2	1.9
Pd	-	0.45	0.3
Re	-	-	2.3



**Fig. 1.** High-resolution N 1s XPS spectra of the SiO<sub>2</sub>/Si substrate after: (a) modification of the substrate by APTMS, and (b) following Pd-citrate activation.

of  $NH_2$  and  $NH_3^+$  are 60–40%, respectively. It has been reported that the formation of protonated amine may be promoted by traces of water and is related to either H-bonding of the  $NH_2$ -groups [18] or to bonding to OH groups on the substrate [19]. After Pd-citrate activation, the protonated peak is less intense, as shown in Fig. 1b. In this case, the curve fitting (not presented here) indicates that the concentrations of  $NH_2$  and  $NH_3^+$  are 78% and 22%, respectively. The reduction in the concentration of  $NH_3^+$  may be attributed to the adsorption of the Pd-ions onto the exposed amino groups with the simultaneous screening of the underlying protonated amine groups that are closer to the SiO<sub>2</sub>/Si-substrate.

The successful activation of the surface was confirmed by the presence of Pd 3d-doublet-structure. Fig. 2a shows the spectrum for the modified SiO<sub>2</sub>/Si substrate activated by Pd-citrate. The Pd-ions adsorbed on the surface were reduced by DMAB in the electroless plating solution, in order to evaluate the oxidation states of Pd when it is introduced into the solution containing the reducing agent. The reduction process was performed under the same conditions as for Bath I (Table 1), without using a metal source and a complexing agent, and with holding time of 40 s. After reduction, as illustrated in Fig. 2b, there is a shift in the Pd  $3d_{5/2}$  peak position from 336.45 eV to a lower binding energy of 335.7 eV related



**Fig. 2.** High resolution Pd 3d XPS spectra of the modified SiO<sub>2</sub>/Si substrate after: (a) Pd-citrate activation process, (b) the following reduction by DMAB, and (c) electroless Re plating.



**Fig. 3.** TEM cross-section image of Pd catalysts that are formed on the modified SiO<sub>2</sub>/Si substrate after activation with Pd-citrate, following reduction by DMAB.

to Pd°, as a result of formation of metallic Pd. Decrease in the full width at half maximum (FWHM) of the Pd  $3d_{5/2}$  peak indicates that Pd is present in the metallic state, while oxidation states are highly reduced. This effect has been reported elsewhere [20] after catalyzing the surface by immersion in a PdCl<sub>2</sub> solution, followed by reduction with DMAB. It is important to note that, in our case, PdCl<sub>2</sub>-citrate activation was performed.

Fig. 3 shows a cross-section TEM image of the reduced Pdcatalysts on the APTMS-modified SiO<sub>2</sub>/Si substrate. The average diameter of the Pd particles is found to be in the range of  $3.2 \pm 1.0$  nm. The surface coverage is 15%.

#### 3.2. Composition and structure of the deposit

Previous studies showed that pure rhenium coating cannot be deposited from electroless plating baths when only perrhenate salt is used [11,15,17]. The addition of Ni or Co is needed to start the induced codeposition of Re. In the current work, the study is extended, and high-resolution techniques, such as HR-TEM and HR-XPS are utilized in order to investigate the formation of a Re film on the surface when only perrhenate salt is used (see Table 1, Bath I).

Electroless plating of Re on modified and Pd-activated surface results in the presence of 2.3 at.% of Re and an increase in the O-content. The latter is related to formation of Re oxides on the surface (cf. Table 2). XPS signals from N and Pd are screened by this oxide layer, hence a slight reduction in their contents is observed, compared to data obtained only after modification and activation procedures (cf. Table 2).

Fig. 4 demonstrates the curve fitting of high-resolution Re 4f spectra in order to evaluate the oxidation state of rhenium on the modified and activated surface. The deposition time was 40 s. The most intensive peaks in the spectrum appear at binding energies of about 41.9 eV (4  $f_{7/2}$ ) and 44.33 eV (4 $f_{5/2}$ ), corresponding to Re 4f doublet with 2.43 eV multiplet splitting between peaks. The binding energy of the  $4f_{7/2}$  peak is higher than that of metallic Re, but lower than that of ReO<sub>2</sub>. Therefore, it may correspond to the Pd–O–Re bonding complex. Similar values for  $4f_{7/2}$  and  $4f_{5/2}$  peaks of 41.6 eV and 44.03 eV, respectively, have been estimated before for the Sn–O–Re state [21]. Our assumption is in good agreement with the Pd behavior shown in Fig. 2c. An increase in the FWHM of the two peaks in Pd 3d doublet structure after Re electroless plating



Fig. 4. HR-XPS Re 4f spectra with curve fitting of the electroless plated Re on modified and activated  $SiO_2/Si$  substrate.

(Fig. 2c), as compared to the Re reduced structure (Fig. 2b), points to increased Pd oxidation after electroless plating.

According to Fig. 4, Re is also found at the surface as metallic Re, ReO<sub>2</sub>, and ReO<sub>3</sub>. The curve fitting indicates that about 14% of rhenium is found as metallic Re, while 15% and 7% are related to the oxide states ReO<sub>2</sub> and ReO<sub>3</sub>, respectively. The metallic Re seems to be formed as a result of reduction of  $\text{ReO}_4^-$  to the lower oxidation states of ReO<sub>3</sub> and ReO<sub>2</sub>, that are further reduced to Re. This reaction sequence has been proposed and discussed previously for the electrodeposition of rhenium thin films from acid baths on noble metals and n-Si (100) substrates [22,23].

Fig. 5a and b shows cross-section TEM images taken after deposition from the Ni-free plating bath (c.f. Bath I, Table 1). It is clear from this figure that a discontinuous layer of Re is formed during electroless plating. This layer becomes somewhat denser with increasing deposition time, from 15 s (Fig. 5a) to 40 s (Fig. 5b), but significant thickness is not achieved. It is important to note that even after relatively long deposition times (>10 min), the Re layer does not continue to grow. The Pd-catalyst that is formed on the modified surface acts as initiator for nucleation sites for the following Redeposition. Therefore, some nucleation sites of Re are formed on the modified and catalyzed surface. The catalytic particles can be considered as carriers in the path of transfer of electrons from the reducing agent to the metal ions in the bath. Thus, the catalytic surface is an important factor for the kinetics [24]. With increasing deposition time, the Pd-particles are covered by Re deposits, and the process of growth seems to be terminated. Most of the Re that is obtained on the surface is in an oxidized state, as shown

in Fig. 4. It may be considered as a catalytically-inactive surface, and as the reason that pure Re coating cannot be obtained using electroless plating. This is in accordance with data obtained in previous studies [15,17]. The deposition rate decreased in electroless plating of CoReP and NiReB as the concentration of ammonium perrhenate in the plating bath was increased. It was claimed that Re has no catalytic effect, and its increased content in the alloy should occur at the expense of Co or Ni. It was also hypothesized that this decrease may be connected to the partly reduced Re compounds in the electroless plated deposits. Consequently, it can be stated that the condition of autocatalysis is not obtained during the electroless plating of Re, unless a Ni salt is added to the plating bath (cf. Bath II, Table 1), and only then the film growth is observed, as illustrated in Fig. 5c. In this case, an 18-nm thick Re–Ni coating is formed (compare to the deposit obtained after the same deposition time of 40 s, which is shown in Fig. 5b).

The Re-Ni film growth evolution and its morphology during deposition are illustrated in Fig. 6. The upper row shows SEM images, while the lower shows TEM cross-section images. The images capture the evolution of the layer from the growth of separate islands, through coalescence, percolation, and finally the formation of a complete layer. The thickness of the layer is calculated from the TEM images, and is summarized in Fig. 7. Points A, B, C, D are correlated to the images shown in Fig. 6. In addition, the surface coverage and Re/Ni ratio are extracted from the top-view SEM images and XPS analyses, respectively, and are presented in the inset of Fig. 7. A two-slope chart is evident, indicating the existence of incubation time and nucleation at the early stage of growth. Until the percolation period (point A–C), film deposition is slower than during continuous film growth. A first continuous layer is seen after about 20 s of deposition, with a thickness of about 7 nm. At this point, the growth rate accelerates to about 30 nm/min.

The TEM images in Fig. 5c show that the Re–Ni layer is nonuniform in density; a darker linear layer is observed at the interface with  $SiO_2$ , which indicates a non-uniform composition of the layer. The change in composition of the layer during its growth is also shown in the quantification of the Re/Ni ratio, see Fig. 7. The Re/Ni ratio is calculated on the basis of the XPS measurements. One can notice that the ratio increases up to the point where the layer reaches full coverage. It appears that the delay of nucleation is controlled by an early formation of a Re-rich layer.

Fig. 8 shows STEM high-angle annular dark-field (STEM-HAADF) cross-section image of Re–Ni layer with a thickness of 23 nm. The image is highly sensitive to variations in the atomic number of the elements in the sample. A higher mass appears brighter in the image and therefore can indicate on Re-rich regions. The inset in Fig. 8 presents a brightness profile taken across the layer (see marked rectangular). The profile can be segmented into three areas: A – the



Fig. 5. TEM cross-section images of: (a, b) Re deposit, (c) Re–Ni deposit, formed from baths containing either only potassium perrhenate or potassium perrhenate and nickel sulfate, respectively. Deposition time: (a) 15 s, (b, c) 40 s.



Fig. 6. SEM (top) and TEM (bottom) cross-section images of Re-Ni films on modified SiO<sub>2</sub>/Si substrates, evolved in time from zero time A (6 s), B (10 s), C (15 s), and D (20 s).

bottom interface presents the highest brightness, hence the highest Re mass concentration in the layer. Area B presents a second additional peak in brightness, and area C exhibits a moderate reduction in brightness. It is evident that the increase in the brightness at the interface with the SiO<sub>2</sub> substrate, areas A and B compared to area C, corresponds to the higher Re-content area.

In addition to the results obtained above, during deposition a change in the color of the surface as a function of deposition time is also noted. As illustrated in Fig. 9A, the first layers that are formed within a short deposition time (<20 s) have a blue color, whereas thicker films have a silver-like color. It should be noted that the color in Fig. 9A(b) is different than that of the substrate in Fig. 9A(a). The Re–Ni deposits were also analyzed by XPS and compared by using high-resolution measurements of Re 4f, as shown in Fig. 9B. The measurement was performed at 75° take-off angle in order to obtain signals from deeper parts of the sample, and thus to eliminate the effect of surface oxides. Although the Re-to-Ni ratio is reduced for longer deposition times (see Fig. 7), the XPS data in Fig. 9B shows that the amount of metallic Re is increased at longer

deposition times. For short deposition times (Fig. 9B), most of the Re that is formed is in oxidized states, as evident by the blue surface. Based on these results, it can be concluded that the reduction of  $\text{ReO}_4^-$  ions involves rhenium oxides ( $\text{ReO}_2$  and  $\text{ReO}_3$ , based on the XPS data) prior to deposition of metallic Re. Thus, in addition to the metallic Re, the higher Re-content is also associated with formation of Re-oxides. The results shown in this paper are in accordance with the mechanism proposed on the basis of the electrochemical study for the electrodeposition of rhenium from an alkaline aqueous solution (pH 13.3) [25].

The XRD pattern for an as-deposited Re–Ni film with a thickness of 18 nm is shown in Fig. 10b. In the range of  $35^{\circ} < 2\theta < 50^{\circ}$ , a peak related to the formation of a Ni–Re phase is evident. The same peak was attributed to as-deposited amorphous electroplated Ni–Re films [26]. The peak at  $2\theta \approx 56^{\circ}$  is related to the Si-substrate. Additional peaks, at  $2\theta \approx 16.6^{\circ}$  and  $2\theta \approx 25.3^{\circ}$  are also observed. These peaks may be attributed to the H<sub>0.57</sub>ReO<sub>3</sub> phase, based on comparison to XRD patterns reported elsewhere for powders of ReO<sub>3</sub> reacted with hydrogen [27]. Moreover, the same peaks are



Fig. 7. Thickness of the Re-Ni films vs. deposition time. The effects of deposition time on the surface coverage and Re-to-Ni atomic ratio are also demonstrated.



**Fig. 8.** STEM-HAADF image of a Re–Ni layer with a thickness of 23 nm. Brightness variation along the layer is the result of local variation in the concentration of Re.

also observed in as-deposited deposits when only a perrhenate salt is used in the electroless plating bath, see Fig. 10a. In order to evaluate the effect of aging, the sample in Fig. 10b was left in ambient air for 2 weeks to 1 month, acquiring immediately afterwards XRD data (Fig. 10c and d, respectively). A change is evident in the diffraction patterns as a function of exposure time. The intensities of the peaks at  $2\theta \approx 16.6^{\circ}$  and  $2\theta \approx 25.3^{\circ}$  increase as a result of aging. In addition, new reflections are apparent; these are associated to the H<sub>0.57</sub>ReO<sub>3</sub> phase. Moreover, the Ni-Re reflection is shifted to lower reflection angles and becomes less intense. Thus, based on Fig. 10c and d, the electroless Re-Ni layers are not chemically stable in air at room temperature, and seem to be oxidized and undergo hydrogen intercalation and consequent transformation to the H<sub>0.57</sub>ReO<sub>3</sub> phase. This effect can be attributed to a high hydrogen evolution rate during deposition of high Re-content alloys, and thus to the absorption of hydrogen in the coating during deposition. Moreover, the fine-grained structure of the Re-Ni deposits that are formed during deposition can also accelerate the degeneration of the coating. In order to improve the stability of such layers, thermal treatment is required.

The observation of the  $H_{0.57}$ ReO<sub>3</sub> phase is interesting. It has been reported that most of the thin films of ReO<sub>3</sub> deposited by thermal evaporation and sputtering consist of a rhenium-hydrogen phase.



**Fig. 10.** XRD spectra of electroless plated: (a) Re, (b) Re–Ni, after 40 s of deposition (c, d) are the diffraction patterns of sample (b) after aging in air (ambient environment) for 2 weeks and 1 month, respectively.

This disordered  $H_x$ ReO<sub>3</sub> phase was proposed for solid-state battery and liquid-crystal cell applications due to its high ionic and electronic conductivities [28,29]. The process used in this study is simpler and may offer an attractive route for preparation of  $H_x$ ReO<sub>3</sub>



Fig. 9. (A) CCD camera images of: (a) SiO<sub>2</sub> substrate, (b, c) Re–Ni deposits after 18 s and 40 s deposition, respectively. (B) HR-XPS spectra of Re 4f in Re–Ni deposits obtained after 18 s and 40 s.



Fig. 11. Sheet resistance (squares) and inverse sheet resistance (circles) of Re–Ni films deposited on the modified and activated  $SiO_2/Si$  substrate as a function of film thickness.

coatings. However, further work is required to properly demonstrate it.

The electrical properties of as deposited Re-Ni thin films were also measured. Fig. 11 shows the measured sheet resistance values of the Re-Ni layers deposited on modified and activated SiO<sub>2</sub>/Si substrate, as a function of film thickness. The sheet resistance of the Re-Ni allov lavers decreases as the film thickness is increased. For Re-Ni films thinner than 18 nm, the resistance increases abruptly from 1160  $\Omega$ /sq. at 18 nm to 4570  $\Omega$ /sq. at 7.5 nm. These high values of sheet resistance can be related to the formation of the Re-oxides, in addition to the metallic Re, on the surface of the SiO<sub>2</sub> substrate. Re–Ni deposits thicker than 18 nm show a sharp decrease in the sheet resistance. The sheet resistance of even thicker films (between 25 and 30 nm) decreases from  $302 \Omega/sq$ . to 211  $\Omega$ /sq. These are relatively high sheet resistance values, probably due to the high Re-content in the films. From Fig. 11, which shows the inverse sheet resistance, it can be estimated that a non-uniform layer is formed. Two slopes are noticed in this figure, which may be attributed to the formation of two layers with parallel resistor characteristics, when films thicker than 18 nm are deposited.

Over the years, a new generation of the electroless Ni-bath nanocomposite coatings has been proposed, e.g. using second-phase nano-particles such as ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, etc., dispersed in a Ni matrix [30,31]. The formation of a chemically graded layer in the present study may be beneficial too, with respect to the adhesion strength and the mechanical behavior of electroless Re–Ni coatings.

#### 4. Conclusions

In this study, electroless plated Re–Ni layers with high quality and good adhesion were obtained. The process used is simple, employing silanization in ambient conditions, as opposed to the common silanization processes in either a nitrogen atmosphere or vacuum (CVD). Moreover, it was demonstrated that using an "all-wet" technology, from the modification and activation procedures to the formation of Re–Ni coatings, can produce an ultrathin (7 nm) dense layer, without visual defects, with uniform thickness. It was also demonstrated that when only perrhenate salt is used (i.e. in the absence of Ni<sup>2+</sup> ions), the surface coverage of Re particles was not complete, and the layer growth was terminated. In contrast, addition of as low as 3.45 mM Ni<sup>2+</sup> ions to the electrolyte allowed the autocatalytic reaction that is required for electroless plating. As-deposited Re–Ni films consisted of an amorphous Ni–Re phase along with a  $H_{0.57}$ ReO<sub>3</sub> phase. In the case of pure Re deposits, the same  $H_{0.57}$ ReO<sub>3</sub> phase was also detected.

It was found that the chemical composition of the Re–Ni layers was not uniform across the thickness. The Re-content in the layer gradually increases up to its maximal value at the percolation point. In addition, the oxygen content in the deposit is initially higher, possibly indicating on the following route of deposition: reduction of  $\text{ReO}_4^-$  to lower valence oxides, such as  $\text{ReO}_3$  and  $\text{ReO}_2$ , that are further reduced to metallic Re.

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