Coordination-Based Supramolecular Structures on Gold

Thesis for the degree
Doctor of Philosophy

By

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This work was carried out at the Department of Materials and Interfaces, The Weizmann Institute of Science, Under the supervision of Prof. Israel Rubinstein and Prof. Abraham Shanzer.
To my children Nitzan and Alon, my husband Avihay,

My parents Avner and Rachel and my brother Gil,

With Love
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1. Introduction

1.1. Self-assembled monolayers (SAMs)

The concept of monolayers was introduced in 1917 by Langmuir who studied the spreading of amphiphiles on water and realized that the film had the thickness of one molecule. By careful compression of the film a regularly oriented monolayer of molecules could be obtained. Later, Blodgett transferred the monolayer from air-water interface onto solid support (Langmuir-Blodgett (LB) films), and by repetitive transfer, multilayers could also be formed. These LB films are thermodynamically unstable, which means that temperature changes or exposure to solvents can affect their two-dimensional structure. Zisman and co-workers were the first to demonstrate the spontaneous formation (self-assembly, SA) of monomolecular layer by adsorption of alkylamines on platinum substrate. Since then a number of adsorbates have been found capable of forming SAMs on certain substrates, e.g., sulfur-containing adsorbates on gold, chlorosilanes derivatives on glass, and fatty acids on metal oxide surfaces. A common feature of these systems is the chemical interaction between the adsorbate and the substrate. Moreover, van-der Waals interactions between the adsorbate molecules give rise to a dense packing of the monolayer.

Studies on SAMs usually concern basic understanding of their growth and final structure, as well as their applications. The possibility of obtaining desired optical, electrical, and chemical properties in monolayers makes them attractive in electronic, optoelectronic or sensing devices. They may serve as passive layers for corrosion protection, adhesion promotion, optical isolation, and pattern definition. More complex activities can include capacitance, rectification, transistor behavior, photoconduction, sensing and electrooptical switching. Thin films may also be used to the study of molecular recognition events and mimicking of biological functions. Yet, some applications may require more than one molecular layer.

1.2. Supramolecular Multilayers

Extension of the two-dimensional system of SAMs to a three-dimentional system, ca. building of a multilayer, have the advantage of enhancement of the layers properties and creating new classes of materials possessing functional groups at controlled sites. Multilayer construction may be achieved by the LB method, by self-assembly of the layers through covalent bonds or metal-ion coordination, as well as
by gas phase molecular layer epitaxy,\textsuperscript{16,17} plasma deposited films\textsuperscript{18} and layer-by-layer (LbL) deposition method of positively and negatively charged species.\textsuperscript{19-21}

Metal-ion coordination is commonly used in supramolecular chemistry, which deals with organized entities of higher complexity that results from the association of two or more chemical species held together by intermolecular forces.\textsuperscript{22} The driving force for the connection between the chemical species is "molecular recognition", which causes a molecule or ion to selectively, and usually noncovalently, bind to a complementary host.\textsuperscript{23} Thus, self-assembled multilayers based on metal-ion coordination are a viable possibility for supramolecular structures built on a solid support.

The use of metal ions as coordination links between molecular layers may result in an ordered system wherein the structure as well as electronic and optical properties may be varied by choice of the metal ion. The ligand molecules involved in such a structure allow structural versatility and may impart various mechanical, electrical and optical properties.\textsuperscript{24-26} The use of a solid support for the supramolecular structure presents various opportunities, for example signal transduction and catalysis. Moreover, a conducting support provides electrical contact to the assembly; hence, metal substrates (especially gold) are often used as substrates in such systems.\textsuperscript{24-27}

Recently it was shown\textsuperscript{28} that a novel kind of SA organic multilayers, based on metal ion coordination, can be constructed in a stepwise manner: formation of a ligand monolayer, coordination of tetravalent metal ions to generate a monolayer of metal-organic complexes, bonding of a second ligand layer possessing two ion-binding sites to the first metal-ion coordinated layer, while forming a free site for a second metal-ion layer, and repeating this process to form a multilayer (Fig. 1). The procedure enables controlled layer-by-layer construction of three-dimensional metal-organic multilayers and superlattices of substantial variability, upon varying the first ligand layer, the coordinated metal-ions or the organic linkers.

This system is further studied in the present work (section 3.2. and 3.2.1.),\textsuperscript{29} and exploited for the development of a new characterization technique (section 3.1.).\textsuperscript{30} It is also used for evaluation of the sensing capability of ultrathin gold island films (sections 3.3. and 3.4.).\textsuperscript{31,32} Since the process is time-consuming (ca. one day per layer), and therefore impractical for the construction of a large number of layers, an effort was made in this work to construct more than one layer in each step (section 3.2.2.). The construction of a coordination multilayer based on hydroxyquinoline ligand is also
demonstrated (section 3.2.3.). Such multilayer may be of interest for organic light emitting diode (OLED) preparation (see refs. in 3.2.3.).

![Diagram showing coordination-based multilayer construction](image)

**Figure 1:** Coordination-based multilayer construction. 28

### 1.3. Characterization methods

Comprehensive characterization of mono- and multilayers on solid support requires the use of a variety of analytical techniques. The techniques used in this study are described below.

**Wettability measurements** are a simple and effective method for obtaining a first impression on the structure and composition of the layer. 23 The contact angle (CA, Θ), formed by a droplet of a probe liquid on a monolayer-coated surface, is given by the Young equation (γ = γ + γ cos Θ), which relates it to the surface free energy of the solid-liquid (γ), solid-vapor (γ), and the liquid-vapor (γ) interface.

However, Young equation is only valid in the case of a thermodynamic equilibrium, which is practically never achieved during measurements. The deviation from thermodynamic equilibrium results in different CAs during increase and decrease of the drop volume (hysteresis). Advancing CAs (increasing drop volume) are primarily influenced by the polarity of the monolayer. The receding CA (decreasing drop volume) is lower than the advancing CA and is influenced by monolayer packing and defects. The difference between the advancing and receding CA (hysteresis) for well-packed alkyl monolayers is on the order of few degrees and increases to values above 30° for disordered layers. Although the hysteresis is sensitive to the degree of order in
the underlying monolayer, a quantitative interpretation is difficult since the surface roughness and defects contribute to the hysteresis.\textsuperscript{34}

\textit{Ellipsometry} is the most common optical technique for estimating the thickness of thin organic films. It is based on a polarized light beam that is reflected from the substrate, resulting in a change of the phase ($\Delta$) and amplitude ($\Psi$) of the light.\textsuperscript{34} Usually obtaining these two parameters for the uncovered and covered substrate allows calculation of the thickness and the refractive index of the film. However, if the film has a thickness below $1/10^{\text{th}}$ of the wavelength of the incident light, the changes in $\Psi$ are too small and a value for the refractive index is needed.\textsuperscript{35} Usually refractive indices between 1.45 and 1.50 are used for organic SAMs, which are close to the values for bulk alkanes. Ellipsometry is a convenient method for following the construction of a multilayer and is used for this purpose in the present as well as in our previous studies.\textsuperscript{26,28,36}

\textit{UV-Vis absorption spectroscopy} can be used to analyze monolayers of chromophoric molecules. The intensity of the absorption bands can be related to the surface density of adsorbate by the of Beer-Lambert law: $A=\varepsilon \rho$, where $\rho$ is the surface density, $A$ is the absorbance of the SAM, and $\varepsilon$ is the molar absorption coefficient. Usually, the absorption coefficient of an adsorbate in a SAM is not known, hence values obtained from solution studies are used. However, the restricted rotational freedom of the adsorbate and the polarity of the monolayer might influence the absorption coefficient.

\textit{Transmission surface plasmon resonance (T-SPR) spectroscopy} is a new method based on measuring the surface plasmon (SP) absorption band of ultrathin evaporated gold island films using transmission UV-vis spectroscopy.\textsuperscript{37} The SP absorption characteristic of such films is highly sensitive to the surrounding medium, with the plasmon band changing in intensity and wavelength upon binding of various molecules to the surface. The binding process can be monitored quantitatively by measuring the changes in the gold SP absorption in transmission UV-vis spectroscopy. T-SPR spectroscopy have been shown to be applicative to both chemically and physically adsorbed molecules, in liquid or gas phase, with measurements carried out either ex situ or in situ. The sensitivity of T-SPR spectroscopy in detecting molecular binding to the gold depends strongly on the Au film preparation conditions, a subject which is further studied in this thesis (section 3.3. and 3.4.)\textsuperscript{31,32} in order to get the optimal
sensitivity. Another important issue studied in this thesis (section 3.4.) is the sensitivity of the SP as a function of distance from the surface, which is important for sensing applications.

**X-ray photoelectron spectroscopy (XPS)** is a surface analytical technique in which the sample is irradiated with monochromatic X-rays, leading to the emission of core electrons (photoelectrons). An analyzer collects the escaping photoelectrons and measures their abundance as a function of their kinetic energy. The kinetic energy is defined by the energy of the X-rays ($E_{\text{X-rays}}$), the binding energy of the electron ($E_b$), and the workfunction of the spectrometer ($\Phi$):

$$E_{\text{kin}} = E_{\text{X-rays}} - E_b - \Phi$$

Since the binding energy depends on the element and its oxidation state, XPS can be used to determine the elemental composition of the outer few nanometers of solid samples. By detecting the photoelectrons under large angles from the surface normal, the electrons originating from atoms close to the surface will be enhanced relative to those from atoms deeper in the layer. Hence, angle-dependent XPS measurements can be used to determine the vertical position of elements is SAMs. Yet, this method requires a large number of measurements (which may induce damage), and is strongly model-dependent. The position of elements (depth profile of the layer) may be studied also by ion-etching, which is inherently destructive and limited in application, particularly with soft matter. Another depth profiling method, Tougaard's approach, is based on quantitative analysis of signal-to-background correlation. This method requires minimal interference of neighboring lines across a wide spectral range, and is therefore less effective with small signals. The drawbacks of the presented methods and the depth sensitivity of the XPS led us to the development of a new XPS depth profiling method, entitled Controlled Surface Charging (CSC) (section 3.1.).

**AFM** probes the surface of a sample with a sharp tip, several of microns long and often less than 10 nm in diameter. The tip is located at the free end of a cantilever that is 100 to 200 μm long. Forces between the tip and the sample surface (the most common, but not the only one, is the van der Waals force) cause the cantilever to bend, or deflect. A laser detector measures the cantilever deflection as the tip is scanned over the sample (or the sample is scanned under the tip). The measured cantilever deflections allow to generate a map of surface topography.
Regarding the van der Waals force, the AFM may be operated in contact, non-contact or intermittent contact modes. In the contact regime, the AFM tip makes soft "physical contact" with the sample, ca. the cantilever is held less than a few angstroms from the sample surface, and the interatomic force between the cantilever and the sample is repulsive. Contact mode AFM often has a disadvantage for samples that are either weakly bound or soft because the tip can damage the surface features. In the non-contact regime, the cantilever is held on the order of tens to hundreds of angstroms from the sample surface, and the interatomic force between the cantilever and the sample is attractive. The total force between the tip and the sample in this mode is very low (~ $10^{-12}$ N), which is advantageous for studying soft or elastic samples. Another advantage of this mode is lack of tip and sample degradation, effects which may happen in the contact mode. In the intermittent contact regime the cantilever tip is brought closer to the sample so that at the bottom of its travel it just barely hits, or "taps", the sample.

In both intermittent and non-contact regimes, the system vibrates a stiff cantilever near its resonant frequency with an amplitude of a few tens to hundreds of angstroms (AC detection scheme). It detects changes in the resonant frequency or vibration amplitude as the tip gets near the sample surface. In acoustic AC mode (AAC mode), the cantilever is excited by high frequency acoustic vibration from a piezoelectric transducer attached to the cantilever holder.

*Electron microscopes (EM)* use a focused beam of electrons to image the specimen and gain information as to its structure and composition. The basic steps involved in all EMs are: (i) a stream of electrons is formed and accelerated towards the specimen using a positive electrical potential; (ii) this stream is confined and focused using metal apertures and electromagnetic lenses into a thin, focused monochromatic beam; (iii) the beam is focused onto the sample using an electromagnetic lens; (iv) interactions occur inside the irradiated sample, affecting the electron beam. These interactions and effects are detected and transformed into an image.

The interactions of the electron beam and the specimen, which provide the detected signal, are shown in scheme 1. The ones noted on the top-side of the scheme are utilized when examining thick or bulk specimens, using *Scanning Electron Microscopy (SEM)*. The ones on the bottom side of the scheme are those examined in thin or foil specimens, using *Transmission Electron Microscopy (TEM)*.

6
Scheme 1.

In SEM, the production of secondary electrons is topography related, while the backscattered electrons are utilized to differentiate parts of the specimen that have different average atomic numbers. Auger electrons and X-rays give compositional information about the specimen.

In TEM, the transmission of unscattered electrons is inversely proportional to the specimen thickness. Areas of the specimen that are thicker will have fewer transmitted unscattered electrons and so will appear darker than thinner areas. Elastically scattered electrons can yield information on orientation, atomic arrangement and phases present in the area being examined. Inelastically scattered electrons can be used to extract both compositional and bonding (i.e. oxidation state) information on the specimen region being examined.

As in traditional microscopy, the wavelength of and the ability to focus the incident beam - in this case a beam of electrons- determine the microscope resolution. **High-Resolution-SEM (HR-SEM)** is based on a cold field emission gun (CFEG) electron source. The CFEG and the semi-intens objective provide high-resolution images. **HR-SEM** was used in this thesis to study the morphology of evaporated gold island films, before and after multilayers assembly (sections 3.3. and 3.4.). HR-**TEM** was used here to elucidate the phase of zirconia layer formed on organic SA monolayer (section 3.2.).

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1.4. The substrate

The various methods mentioned above have different requirements from the substrate that supports the ultrathin overlayer. In the case of gold, which is the substrate used in the present work, one finds:

(a) Ellipsometric measurements of SAMs are usually preformed using thick (typically 100-300 nm), reflective Au films evaporated on flat substrates (e.g., highly polished Si).\textsuperscript{41}

(b) Transmission spectroscopy of SAMs requires continuous ultrathin (transparent) Au films deposited on transparent substrate.\textsuperscript{42} For T-SPR spectroscopy the gold should be transparent and in the form of islands, since the measured signal is characteristic of the gold islands and disappears when the gold becomes continuous.\textsuperscript{32,37}

(c) AFM and STM imaging of monolayers is preferably done on atomically flat surfaces. The most widely used is gold evaporated onto heated mica.\textsuperscript{43-45} Another substrate is a single-crystals Au beads prepared by the method of Clavilier et al.\textsuperscript{46-50} The beads have (111) facets formed during crystallization, in which atomically flat terrace-step structures are consistently observed. Although more difficult to handle, the gold beads provide higher resolution images of monolayers (section 3.2.1.).
2. Research overview

My PhD work aimed at the study of self-assembled coordination-based metal-organic multilayers on gold surfaces. Emphasis was put on detailed analysis of multilayer structures, including the development of a new characterization technique (sections 3.1. and 3.2.). The main ligand used was hydroxamate, while the ability to construct multilayers using hydroxyquinoline ligands was also demonstrated (section 3.2.3.). Zr(IV) and Ce(IV) were mostly used as binding ions. The construction of the multilayers was carried out as previously published by our group\textsuperscript{28} (alternate adsorption of organic layers and metal ions). However, we show here preliminary results on the formation of multilayers by a pseudo-polimerization process (section 3.2.2.). Various gold substrates (continuous and island-type) were used as the solid support. Continuous gold films (100 nm evaporated gold films on highly-polished silicon, or gold beads (section 3.2.1.)) were used for the analysis of the multilayer structures, whereas gold island films coated with coordination multilayers were used to evaluate the distance sensitivity of T-SPR spectroscopy\textsuperscript{37,51} (sections 3.3. and 3.4.).

More specifically the thesis includes:

- The development of a method for probing the structure of ultrathin layers, several nanometers thick (section 3.1.).\textsuperscript{30} XPS was the method of choice; the objective was to find a direct way to obtain vertically resolved structural information from the raw XPS data. For the demonstration of the method we used self-assembled coordination-based metal-organic multilayers on gold surfaces (100 nm Au evaporated on silicon). The construction was done layer-by-layer as described previously by our group\textsuperscript{28}, while here we also inserted diphosphonate and Hf(IV) layers as markers at predetermined depths. In the new method the surface of the dielectric overlayer is charged with the XPS electron flood gun, creating a controllable potential gradient. The local potential is probed by measuring XPS line shifts, which correlate directly with the vertical position of the atoms. We termed the new method 'Controlled Surface Charging' (CSC) and used it further to study the electric properties of similar multilayer structures (section 3.2.).\textsuperscript{29} We expect the method to be applicable to a large variety of mesoscopic heterostructures.

- The effect of the binding-ion on the structural, mechanical and electrical properties of the multilayers was studied (section 3.2.).\textsuperscript{29} In this part of the work we
found that using ethanolic ZrCl$_4$ solution as the source of the binding ion, as was done in previous work$^{28}$, brings to the formation of a composite multilayer with zirconia-type deposit between the organic layers. In contrast, using zirconium acetylacetonate for the binding ion solution (a procedure which was established in the present work) led to the formation of nearly stochiometric 1:1 ligand to metal-ion complex. AFM was used to study the structural and mechanical properties of the multilayers. XPS was used both in the traditional intensity mode, to study the stoichiometry of the multilayers, as well as in the CSC mode, which is sensitive to the electrical conductivity of the multilayers. Ellipsometry and contact angle measurements are used for basic characterization of the multilayers after each binding step. The gold substrate used here was 100 nm gold evaporated on silicon.

- Topography changes of the surface, induced by the first steps of multilayers construction, were studied. Here we used gold beads as substrates, as they provide atomically flat surfaces which enable high-resolution imaging by AFM (section 3.2.1.).
- We show preliminary results on the construction of coordination-based multilayers by a pseudo-polymerization process, which may accelerate the construction of multilayers (section 3.2.2.).
- We demonstrated the use of hydroxyquinoline as ligand in coordination-based multilayer construction schemes (section 3.2.3.).
- Island-type gold films, prepared by evaporation of 1.0 to 15.0 nm (nominal thickness) gold at a rate of 0.005-0.01 nm s$^{-1}$ onto glass substrates modified with 3-mercaptopropyl trimethoxysilane (MPTS), were studied (section 3.3.).$^{32}$ This type of gold films, showing a characteristic surface plasmon (SP) absorption band,$^{37,51}$ is of interest for a variety of sensing applications. The morphology of the films, either annealed or unannealed, was studied by AFM and high-resolution scanning electron microscopy (HR-SEM). The optical properties of the films were examined by transmission UV-Vis spectroscopy, showing a strong dependence of the localized SP band on the morphology of the island films.
- A critical issue in applying T-SPR spectroscopy to chemical and biological sensing is the distance dependence of the localized SP extinction of the gold island films. The system of coordination-based self-assembled multilayers studied in this thesis was used to evaluate the distance sensitivity of T-SPR spectroscopy$^{37,51}$ of gold island films (1.0-5.0 nm nominal thickness) evaporated on silanized glass substrates.
(section 3.4.). This system provides distance tuning in the range from \(-1\) to \(-15\) nm. The morphology of the Au/multilayer system was studied by AFM and HR-SEM, the composition of the system was inspected by XPS and its optical properties were studied by transmission UV-Vis spectroscopy. We showed that by changing characteristic substrate parameters, i.e. Au nominal thickness and annealing, we can vary the distance sensitivity of T-SPR spectroscopy. More specifically, we demonstrated effective sensitivity up to a distance of at least 15 nm when using 5 nm annealed Au island films.
References:

(20) Decher, G. Science 1997, 277, 1232-1237; and refs. therein.


(32) Doron-Mor, I.; Barkay, Z.; Filip-Granit, N.; Vaskevich, A.; Rubinstein, I. Accepted to Chem. Mater.


3. Publications

3.1. *Controlled Surface Charging as a Depth-Profiling Probe for Mesoscopic Layers*  


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Reprint
Controlled surface charging as a depth-profiling probe for mesoscopic layers

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Probing the structure of material layers just a few nanometres thick requires analytical techniques with high depth sensitivity. X-ray photoelectron spectroscopy (XPS) provides one such method, but obtaining vertically resolved structural information from the raw data is not straightforward. There are several XPS depth-profiling methods, including ion etching, angle-resolved XPS (ref. 2) and Tougaard’s approach,7 all but suffer various limitations. Here we report a simple, non-destructive XPS depth-profiling method that yields accurate depth information with nanometre resolution. We demonstrate the technique using self-assembled multilayers on gold surfaces; the former contain “marker” monolayers that have been inserted at predetermined depths. A controllable potential gradient is established vertically through the sample by charging the surface of the dielectric overlayer with an electron flood gun. The local potential is probed by measuring XPS line shifts, which correlate directly with the vertical position of atoms. We term the method ‘controlled surface charging’, and expect it to be generally applicable to a large variety of mesoscopic heterostructures. Charging is commonly considered an experimental obstacle to the quantitative determination of binding energies in XPS measurements of poorly conducting surfaces. To compensate the extra positive charge (a natural consequence of photoelectron emission) and to stabilize the energy scale on a reasonably correct value, an electron flood gun is routinely used, creating a generally uniform potential across the studied volume. This, however, is impossible with systems comprising components that differ in electrical conductivity. In such cases, chemical information may be smeared due to XPS line shifts that follow local potential variations. On the other hand, this very effect can be used to gain structural information.9,12,13 We have shown recently that surface charging can be used to analyse self-assembled monolayers on heterogeneous substrates, providing lateral resolution on a scale given by the substrate structural variations—that is, much smaller than the probe size.9 Here we show that controlled surface charging (CSC) can be applied to obtain nanometre-scale depth resolution in laterally homogeneous structures.

Well-defined correlation between the local potential and the vertical (depth) axis can be achieved in some systems; for example, those consisting of an insulating overlayer on a metallic (grounded) substrate, where the overlayer is laterally uniform. We use such a system in the work reported here. In the present application the flood electron gun is not used for charge neutralization, but rather is operated at a considerably higher flux of electrons this creates a dynamic balance between charge generation and discharge rates, which is controlled by variation of the flood-gun parameters (that is, electron flux and kinetic energy). Evidently, the extra negative charge is accumulated on the film surface, and a dynamic steady state is reached where the charge leakage to the grounded substrate is balanced by the net incoming flux. With the systems studied here, essentially no space charge is developed within the dielectric film. The resultant vertical field is therefore constant, such that the local potential, correlated directly with XPS line shifts, varies linearly with the depth scale (z), unfolding the spectrum with respect to the vertical scale. The steady-state situation, with a surface charge density ρ and an overlay dielectric constant ε, is thus modelled by a parallel-plate capacitor, where the local potential ϕ between the plates is given by equation (1) (ϕ is determined by the overlay resistivity and the flood-gun operating conditions).

\[ \phi(z) = 4 \pi \rho z / \varepsilon \] (1)

The studied substrates comprised a 100-nm [111] textured gold layer, evaporated on a highly polished doped Si[111] wafer. Metal-organic coordinated multilayers were constructed layer-by-layer on the gold surface as previously described. The base layer was a disulphide-bis(hydroxamate) molecule (compound 1 in Fig. 1d). Two different bifunctional ligand repeat units were used, a tetrahydroxamate (2, Fig. 1d) and a diphasphate (3, Fig. 1d)16-18, connected by three different tetravalent metal ions: Zr4+, Ce4+ or Hf4+. XPS measurements were performed on a Kratos Analytical AXIS-HS instrument, using a monochromatized Al (Kα) source (hv = 1,486.6 eV) at a relatively low power in the flood gun was used under varying conditions, of which four are presented here (see Fig. 2 legend). Absolute determination of line shifts was achieved by graphically shifting lines until a statistically optimal match was obtained. This procedure, correlating the full line shape (100–200 data points), allowed excellent accuracy (∼0.03 eV) in the determination of energy shifts, much beyond the experimental energy resolution (that is, source and bare line widths). In cases where the external charging induced line-shape changes, larger uncertainties were considered. The shifts were translated to potential differences relative to the gold by subtracting the corresponding gold shifts. Special effort was made to determine time periods characteristic of the stabilization of local potentials, which were generally longer for the lower flood-gun flux. This was of particular importance in view of beam-induced damage, which was observed after an hour or more and found to slightly distort the CSC behaviour.

The latter will be discussed elsewhere.

For a general demonstration of CSC, two sets of multilayers with varying thicknesses (2 to 10 layers) were constructed (Fig. 1a), using the tetrahydroxamate ligand 2. Each set was assembled with a different binding ion, that is, Zr4+, Ce4+ or Cu4+, respectively. The spectral response to the flood-gun flux is shown in Fig. 2a. The various surface elements manifest energy shifts and line-shape changes, both associated with the development of vertical potential gradients; the Au 4f/line shifts by a very small amount, attributed to the finite (sample-dependent) conductivity of the silicon substrate. All other overlay elements exhibit much larger shifts, with differences correlated with their spatial (depth) distribution. The energy shifts and line shapes of elements not shown in Fig. 2 (N, O) are fully consistent with the model.

In these two sets of samples, all the overlay elements (except sulphur) are distributed along the vertical scale. This complicates the derivation of local potentials in general, and specifically the overall potential difference, \( V_0 \), developed across the entire overlay. (\( V_0 \) here is relative to the 'gun-off' situation.) Yet an approximate analysis can be performed by curve-fitting the metal ion peaks to sets of discrete signals, corresponding to ion interlayers at
Figure 1 Schematic representation of the studied multilayer systems. In panels a–e each 'molecular column' represents a full multilayer, bound to the Au substrate through disulphide groups. The bold symbols represent the marker units. In d are shown the meanings of the symbols used in these column diagrams. The numbers above the columns in b and e indicate the position of the 'moving' marker (abscissa in Fig. 4).

progressive vertical positions. The Zr 3d doublet in Fig. 2a indeed exhibits asymmetric broadening under the 'gun-on' conditions, in contrast with the 'gun-off' situation where potential gradients (of opposite sign) are much smaller, thus having minimal effect on the line shape. (A detailed discussion of potential gradients developed under 'gun-off' conditions will not be given here.) The curve fitting of the 'gun-on' line (Fig. 2a) yields energy shifts of 0.18 eV per layer and an intensity attenuation factor of 1.72 per layer, in good agreement with further results given below. Hence, even without elaborate curve fitting, the Zr (and similarly, the Ce) line can provide an approximate value of $V_0$ from the shift of the low-binding-energy side of the line (rather than the peak), corresponding to the uppermost layer with the largest shift. (The potential gradient in the 'gun-off' situation is much smaller, $-0.035$ eV per layer (from curve fitting of the 'gun-off' lines, not shown). Consideration of these small gradients would increase the derived $V_0$ values by $\pm 10\%$.)

The results, presented as $V_0$ versus multilayer thickness (the former derived from the Zr 3d low-binding-energy side), are shown in Fig. 3. Two important conclusions are drawn from these results. First, the potential difference across the full overlaver, $V_{\text{pol}}$, increases linearly with the layer thickness, suggesting that the layer is practically free of space charge. The system may, therefore, be satisfactorily simulated by the simple electric circuit shown in Fig. 3 inset. Second, the absolute gradient values, associated with the vertical film resistivity, are medium-sensitive; the nearly three-fold difference in the slope of $V_0$ versus film thickness for Zr(v) and Ce(v) suggests a marked influence of the binding ion on the electrical conductivity of the layer, an issue of substantial interest but beyond the scope of this work (complementary characterization, not described here, precludes structural imperfections as a possible cause of conductivity differences). This emphasizes the power of the CSC method in analysing electrical properties of ultrathin films.

We show the enhanced accuracy of CSC depth profiling with two additional sets of tetrahydramate-based coordination multilayers, where the energy shift of an indicator atom, installed at a well defined depth, is normalized to $V_{\text{pol}}$, eliminating the effect of conductivity on the geometric information. Both sets comprised 11-layer films (including the base layer), with Zr(v) as the binding ion. A full quantitative treatment is achieved when two markers are used (Fig. 1c); the value of $V_0$ is accurately determined with a diposphonate layer positioned at the film top, while Hf(v) serves as the 'moving' marker, replacing a Zr(iv) layer at varying depths (a third marker is always the Au substrate). The second set was designed to confirm the compatibility (structural and electrical) of diposphonate linkers with the tetrahydramate multilayer, diposphonates, inserted at progressive depths (Fig. 1b), serve as the marker layer, while Hf(v) is derived (as above, see Fig. 2b) from the shift of the low-binding-energy side of the Zr(iv) line. Diposphonate bilayers, rather than monolayers, were used (except for the top position) (Fig. 1b), in order to increase the P signal intensity.

Selected spectra are presented in Fig. 2b. The complete results, summarized in Fig. 4, show linear behaviour of the normalized shifts, yielding values within 5% of the expected geometric positions (10% for the samples with Hf(v) in position 2). Hence, the energy shifts can be directly converted to depth information on a linear scale and with an accuracy on the order of a single layer thickness in the present case $\approx 1$ nm. The results again justify the use of the

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simple capacitor model suggested above for the local potential in these systems. Moreover, the agreement between the two sets shows the reliability of the CSC method.

To compare these results with the traditional intensity-based depth profiling, the P, Hf and Au line intensities were quantified. As shown in Fig. 4, good exponential dependence is obtained for the intensity ratios, indicating the high regularity of the studied structures, as previously reported. The excellent agreement between the two independent depth-profiling approaches serves to substantiate the CSC results. We note the in situ derivation of the attenuation factor obtained from Fig. 4, \( d/\lambda = 0.54 \), where \( d \) is the single layer thickness and \( \lambda \) the relevant inelastic mean free path (at kinetic energies of 1,300–1,400 eV), calculated here to be 2.73 nm. This value of \( \lambda \) is relatively small compared with values reported for organic media, a result believed to originate from the presence of the metal ions.

Compared to common XPS depth-profiling methods, the CSC-based depth analysis offers several advantages. Ion etching is inherently destructive and limited in application, particularly with soft matter. Angle-resolved XPS (ARXPS), considered non-destructive, is hampered when applied to non-planar morphologies, as it requires a large number of measurements (which may induce...

Figure 2 Spectral response to the electron flood-gun flux. a, A 10-layer multilayer on gold with Zr(4f) lines (Fig. 1a, right). Line-shape changes in the Zr 3d doublet are shown, comparing flood-gun conditions 0 and 2 (see below), the former shifted by −1.66 eV (solid line). Curve fitting of 2 (gun-off) is shown, using three free parameters for the individual Gaussian and only two parameters (interlayer shift and attenuation) to correlate the three doublets, corresponding to the discrete ion layers. Insets, raw data of representative elements at flood-gun conditions 0 and 2. b, An 11-layer Zr(4f)-based multilayer with two markers, Hf(4f) and the diphosphonate 3 (Fig. 1c), with the Hf(4f) in layer no. 4. Raw data of representative elements are shown, at flood-gun conditions 0, 1 and 3. Curves 3 correspond to flood-gun condition 3 for a similar multilayer with the Hf(4f) in layer no. 6. Flood-gun conditions are as follows: 0, gun off; 1, 1.50 mA, −1.5 V (emission current and bias voltage, respectively); 2, 1.90 mA, −2.7 V; 3, 1.90 mA, −3.2 V.
and is strongly model-dependent. Tougaard's approach (quantitative analysis of signal-to-background correlation) requires minimal interference of neighbouring lines across a wide spectral range, and is therefore less effective with small signals. CSC is basically non-destructive, allowing fast and convenient data collection. It enables differentiation of spectrally identical atoms at different locations. It is applicable to thicker structures than ARXPS, as the signal is not subject to increased attenuation associated with off-normal measurements. Substrate roughness, severely affecting ARXPS depth analysis by smearing the angular scale, would only have a minor effect on CSC depth profiling. The linear dependence on depth, found in the present systems, is an attractive feature of CSC. Note, however, that other systems may involve more elaborate conduction processes, possibly causing deviations from linearity. Such deviations may allow the exploration of additional characteristics of the systems, such as charge distribution and conduction mechanisms.

As a high-resolution depth-profiling method, CSC is applicable to a large variety of non-conducting layers less than about 10 nm thick. Moreover, the present results suggest applications of CSC as a contactless electrical probe, capable of direct detection of local potentials in thin overlayers. In the light of recent progress in enhancing XPS lateral resolution, CSC may be an effective tool for studying three-dimensional nanostructures and molecular architectures.

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**Figure 3** Plot of $v_{	ext{d}}$ versus overlayer thickness. $v_{	ext{d}}$ is the total potential difference across the overlayer, and the overlayer thickness is given as the number of molecular layers. $v_{	ext{d}}$ is derived from the low-binding-energy side of the peaks of the respective ions. Inset, the electrical analogue of the overlayer, with a simple parallel-plate capacitor and a shunt resistor.

**Figure 4** Depth profiling with accurately positioned markers. Solid lines show the normalized local potential of the 'moving' marker $v_{	ext{d}}/v_{	ext{d}}$ versus marker position, for P and Hf markers in the multilayer shown in Fig. 1b and c, respectively (linear scale). Dashed lines show depth analysis via line intensities for the multilayer shown in Fig. 1c (log scale). The films with HfN in position 2 (Fig. 1c, left) displayed weak Hf signals that required second-derivative data processing for reliable determination of the energy shifts.

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**Signatures of granular microstructure in dense shear flows**

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Granular materials and ordinary fluids react differently to shear stresses. Rather than deforming uniformly, materials such as dry sand or cohesionless powders develop shear bands, narrow zones of large relative particle motion, with essentially rigid adjacent regions. Because shear bands mark areas of flow, material failure and energy dissipation, they are important in many industrial, civil engineering and geophysical processes. They are also relevant to lubricating fluids confined to ultrathin molecular layers. However, detailed three-dimensional information on motion within a shear band, including the degree of particle rotation and interparticle slip, is lacking. Similarly, little is known about how the microstructure of individual grain affects movement in densely packed material. Here we combine
3.2. Layer-by-Layer Assembly of Ordinary and Composite Coordination Multilayers


To be submitted
Layer-by-Layer Assembly of Ordinary and Composite Coordination Multilayers

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Abstract

Coordination self-assembly of bis(hydroxamate)-based metal-organic multilayers on gold employing a layer-by-layer (LbL) approach was investigated. It is shown that the solution chemistry of the participating metal ion has a marked influence on the composition of the multilayers. Use of Ce(III) and particularly Zr(II) solutions in the ion binding step of multilayer construction, leads to multilayers with a near-stoichiometric metal ion-to-ligand ratio, suggesting a structure close to that predicted by the simple coordination self-assembly scheme. On the other hand use of a ZrCl₄ solution as the source of metal ions in the multilayer construction leads to a multilayer with greater thickness and a large excess of Zr(IV), evenly distributed between the organic layers. In the latter case, a ratio of ca. 1:2 between the excess Zr and oxygen, as well as long-term Zr(IV) binding experiments showing deposition of ZrO₂, suggest the formation of a zirconia-type nanophase between the bis(hydroxamate) organic repeat units.
during multilayer self-assembly. Hence, while the multilayer prepared using Zr(AcAc)$_4$ solution appears to represent a 'true' coordination-based structure, the one prepared using ZrCl$_4$ is best described as a composite organic-ceramic multilayer. Composite multilayers prepared in this way display unusual properties relative to the stoichiometric ones, such as improved dielectric behavior and higher stiffness. Even greater mechanical stability is obtained with multilayers constructed using alternate binding of ZrCl$_4$ and Ce$^{4+}$. The concept of LbL formation of coordination-based composite organic-ceramic structures may be useful in obtaining nanometer-scale structures with special properties.

**Keywords:** Gold, self-assembly, multilayer, coordination, composite, zirconia.
Introduction

Layer-by-layer (LbL) self-assembly, i.e., sequential addition of molecular-size layers to form a complex structure, has been a common way of constructing various nanostructures on flat or curved surfaces. A particularly convenient scheme of this kind is coordination self-assembly, namely, alternate binding of organic ligands and metal ions to form a coordination multilayer. Following the original work of Mallouk and co-workers,1 numerous layered systems based on diphosphonate-terminated organic ligands bound by Zr(IV) or Hf(IV) ions have been studied.2-4 Our group has demonstrated the applicability of this concept to the construction of coordination multilayers based on bishydroxamic acid ligands and tetravalent metal ions. Following self-assembly of an anchor monolayer comprising bishydroxamate-disulfide molecules on gold surfaces, multilayer growth proceeded in a LbL fashion by alternate binding of tetrahydroxamate ligand molecules and Zr(IV), Hf(IV), or Ce(IV) ions.5-7

Systems based on coordination self-assembly generally show regular growth of multilayer structures, as demonstrated using a variety of methods, such as ellipsometry,6,8 wettability,6,8 UV/Vis spectroscopy,9-12 X-ray diffraction,4 FTIR,6,13 XPS,6,7 SPR,14 and others. These studies concentrated on the assembly of organic ligands to form a layered structure, while the mechanism of ion binding as well as the detailed structure have been left largely unresolved. Although the experimental results are consistent with local organization of the multilayers, long-range crystalline order has not been established by direct experimental evidence. The exact stoichiometry of the metal ion-to-ligand ratio in the coordination binding sites has been measured with considerable uncertainty,15 mostly due to the semi-quantitative and model-dependent nature of XPS data. These materials are generally presumed to include a high density of defects of different kinds.5,16

Formation of Zr(IV)-diphosphonate multilayers presents a prominent example of the unsolved mechanism of ion binding. Following the original protocol,1 in most studies binding of Zr(IV) to the phosphonate-terminated surface has been done from 5 mM aqueous (or aqueous-ethanolic17,18) solution of ZrOCl₂, assuming the binding of one Zr(IV) ion per organic ligand. However, details on the structure and stoichiometry of the metal-ion binding site are largely unclear.19 Considering that the predominant forms of Zr(IV) ion in these solutions are tetra- and octa- complexes,20-22 the mechanism of binding of single Zr(IV) ions must include dissociation of polynuclear metal complexes. Direct binding of Zr(IV) tetrarimers to exfoliated α-phosphate particles, continued by diphosphonate ligands, was also suggested.23

Another protocol for the construction of diphosphonate-based metal-organic multilayers involves the use of ethanolic solutions of Zr(IV) acetylacetonate (Zr(AcAc)_4) in the metal-ion binding step.24-27 In this case formation of oligomeric Zr(IV) species in solution is avoided, while the AcAc ligands are readily exchanged by the much more strongly bound phosphonates. Despite the different Zr(IV) chemistry in the aqueous
and ethanolic solutions, the structure of the resulting organic-diphosphonate multilayers is quite similar.

In our earlier studies of Zr(IV)-hydroxamate multilayers we used, in the ion binding step, ethanolic solution of ZrCl$_4$ adjusted to pH 3.3-3.5 with aqueous NH$_2$OH (1-2 vol. %). Adjusting the pH was essential for promoting the replacement of hydroxamic acid protons by Zr$^{4+}$ in the coordination binding site. This protocol enables LbL construction of regular multilayer structures, but leads to uncertainties regarding their composition. Detailed analysis of XPS data for Zr(IV)-bishydroxamate multilayers prepared in this way shows excess of Zr and oxygen compared to the expected values for stoichiometric binding. This result is distinctly different from those obtained with Zr(IV) phosphonate systems, the latter showing no meaningful excess of the metal ion.$^{15,16,27-30}$

The objective of the present work is twofold, i.e., (i) to understand the nature of coordination multilayers prepared using ZrCl$_4$ and showing a large excess of Zr; and (ii) to find preparation conditions leading to bishydroxamate-based coordination multilayers showing Zr(IV):hydroxamate ratios close to the stoichiometric ones, namely, multilayers that conform to the structure shown schematically in Figure 1 and in our previous publications.$^{5-8}$

For this purpose two protocols for Zr(IV) binding and one for Ce(IV) binding during LbL construction of bishydroxamate-metal ion multilayers were tested, using (i) pH-adjusted ethanolic ZrCl$_4$ solution; (ii) ethanolic Zr(AcAc)$_4$ solution; (iii) pH-adjusted aqueous Ce$^{4+}$ solution. It is shown that the use of Ce$^{4+}$, and more prominently Zr(AcAc)$_4$, provides multilayers with metal ion-to-ligand ratios much closer to stoichiometry than those obtained with ZrCl$_4$. The noted excess of Zr and the ca. 1:2 ratio between excess Zr and O in multilayers prepared with ZrCl$_4$, points to the formation of a composite film comprising organic ligand layers spaced by a zirconia-type nanophase. This suggested structure is reminiscent of ultrathin ceramic$^{31}$ and specifically zirconia$^{32,33}$ films prepared on self-assembled monolayers. In the present case the ceramic phase is evenly distributed between the organic layers, suggesting the formation of a new kind of composite nanomaterials. Mechanical and electrical properties of the composite multilayers are shown to be different from those of the stoichiometric ones.

**Experimental Section**

**Chemicals.** Molecules 1, 2, 3 (Figure 1A) were synthesized as previously reported.$^{5,6,8}$ Chloroform (Biolab, AR), was passed through a column of activated basic alumina (Alumina B, Akt. 1, ICN). Ethanol (Merck, AR), H$_2$O$_2$ (Merck, 30%?), NaOH (Merck, AR), HNO$_3$ (Palacid, 69-70%), HCl (Frutarom, 32%), $\text{(NH}_4\text{)}_2\text{Ce(NO}_3\text{)}_6$ (BDH, AR), ZrCl$_4$ (Merck, AR), Zr acetylacetonate (Zr(AcAc)$_4$, Fluka, purum ~98% (uv)) were used as received. Water was triply distilled. Gas used was purified house nitrogen (from liquid N$_2$).
Gold substrates. Gold films, 100 nm thick, were prepared by evaporation onto optically-polished n-type single-crystal (111) silicon wafers (Aurel, Landsberg, Germany), cut into ca. 22x11 mm² slides, as previously described. The Au-covered slides were annealed in air for 3 h at 250°C and left to cool to room temperature.

Multilayer preparation. The Au substrate was pretreated by UV/ozone (using UVOCS T10x10/0ES instrument) followed by ethanol dip, as previously described. Monolayers of the anchor disulfide bishydroxamate 1 were prepared by immersion of pretreated Au substrates in 3 mM solution of 1 in EtOH/CHCl₃ (1:1, v/v) overnight. The slides were rinsed successively with chloroform and absolute ethanol, immersed in ethanol for 20 min and dried under a nitrogen stream. The monolayer was then immersed in 1 mM solution of one of the following: (i) ZrCl₄ in ethanol, pH = 3.3-3.5 (adjusted by addition of 2.5% aqueous ammonium hydroxide) for 10 min followed by ethanol rinse and a 10 min immersion in ethanol; (ii) (NH₄)₂Ce(NO₃)₆ in water at pH = 3.3-3.5 (adjusted by addition of 2.5% aqueous ammonium hydroxide) for 10 min followed by water rinse and a 10 min wash in 1:1 water:ethanol; (iii) Zr(AcAc)₄ in ethanol for 1 h followed by ethanol rinse and a 10-min immersion in ethanol. The resulting metal-organic monolayer complex was exposed to a 3 mM solution of the tetrahydroxamate 2 in ethanol overnight, followed by ethanol rinse, to obtain the second organic layer. The surface was then treated alternatingly with the metal ion and the organic tetrahydroxamate, yielding a multilayer structure. Some of the multilayers were terminated with a layer of the diphosphonate 3 (Figure 1), assembled by immersion in 1.25 mM of 3 in ethanol overnight, followed by ethanol rinse and a 30-min immersion in ethanol. Characterization by ellipsometry and contact angles (CAs) was carried out after each step.

Ellipsometry. A Rudolph Research Auto-EL IV null ellipsometer operating at an angle of incidence of 70° and a wavelength of 632.8 nm was used according to the previously described procedure.

Contact Angle (CA) measurements. Advancing and receding water CAs were measured as previously described, with an accuracy of ±2°. (Bicyclohexyl and hexadecane CAs were not measured, as both solvents wetted the monolayers completely.)

Atomic force microscopy (AFM): AFM images were recorded in air using a Solver P47 (NT-MDT, Rassia) operated in the semi-contact mode. Contact mode was used to form ‘windows’ in the multilayers and for stiffness measurements. The cantilevers used were NSC12 and CSC12 series of ultrasharp silicon (MikroMash, Estonia), with a resonant frequency of 60-200 kHz and an average tip radius of ≤10 nm. Roughness data were extracted from 500x500 nm² images. Average roughness (Rₐ) is reported.

X-ray photoelectron spectroscopy (XPS): XPS measurements were carried out with a Kratos Axis HS XPS system, using monochromatized Al (Kα) X-ray source (1486.6 eV). Except when otherwise indicated, measurements were carried out at normal takeoff angle. Controlled surface charging (CSC) measurements were carried out at two flood
gun settings of the filament current ($I_f$), grid voltage ($V_g$) and filament voltage ($V_f$): (i) $I_f=1.90$ A, $V_g=-4.2$ V, $V_f=-2.0$ V; (ii) $I_f=1.90$ A, $V_g=-3.2$ V, $V_f=-1.5$ V.

High-resolution transmission electron microscopy (HRTEM): HRTEM was performed on a Tecnai F30 (FEI) microscope, equipped with a field emission gun and super twin objective lenses, operating at 300 kV. Images were acquired using a Gatan 1kx1k CCD camera. Image processing was carried out using the Digital Micrograph software. For HRTEM imaging, 15 nm Au films were evaporated at 0.1 nm s$^{-1}$ onto glass substrates at room temperature. The substrate was subsequently annealed in air at 250 °C for 3 h and used for self-assembly. The film was carefully separated from the glass on dilute (~5%) HF solution, and lifted onto a copper grid for HRTEM plan-view imaging.

**Results and Discussion**

**General.** Four different coordination-based multilayers, all composed of the anchor disulfide bis(hydroxamate) molecule 1, the tetrahydroxamate ligand 2, and a binding ion (Zr$^{4+}$, Ce$^{4+}$), were studied (Figure 1). The difference between the four was in the identity and binding protocol of the metal ion: (i) Zr$^{4+}$ bound from a solution of ZrCl$_4$ (denoted ‘ZrCl$_4$’ multilayers); (ii) Zr$^{4+}$ bound from a solution of Zr acetylacetonate (‘Zr(AcAc)$_4$’ multilayers); (iii) Ce$^{4+}$ bound from a solution of (NH$_4$)$_2$Ce(NO$_3$)$_6$ (‘Ce’ multilayers); (iv) a mixed multilayer comprised of alternating layers of ‘ZrCl$_4$’ and ‘Ce’ (‘ZrCl$_4$/Ce’ multilayers). The multilayers were terminated with one layer of the diphosphonate 3, as a marker for accurate measurement of the potential drop over the multilayer ($V_o$) using the controlled surface charging (CSC) method. In addition, ‘ZrCl$_4$’ and ‘Ce’ multilayers without diphosphonate termination (i.e., terminated with the tetrahydroxamate 2) were also studied. The multilayers were constructed on 100 nm Au evaporated onto highly-polished silicon. The samples were characterized by ellipsometry and contact angle (CA) measurements after each step. The completed multilayers were analyzed by XPS both in the traditional intensity mode and using the CSC method. Morphology and stiffness of the multilayers were studied by AFM.

**Basic characterization.** Figure 2 presents ellipsometric data for all the samples (each data point is the average of at least two samples; values for hydroxamate and diphosphonate terminated multilayers are similar). It can be seen that the change in the ellipsometric parameter $\Delta$ in the single-ion samples, i.e., ‘ZrCl$_4$’, ‘Ce’ and ‘Zr(AcAc)$_4$’, increases quite regularly. The total change in $\Delta$ of the ‘ZrCl$_4$’ multilayer is substantially higher than that of the ‘Zr(AcAc)$_4$’ and ‘Ce’ multilayers. In the mixed ‘ZrCl$_4$/Ce’ multilayer a jump in $\Delta$ accompanies each addition of a Zr(IV) layer.

Water CAs were measured for all multilayers after each step in the multilayer assembly, as shown in Figure 3 for ‘Zr(AcAc)$_4$’ multilayer (‘ZrCl$_4$’ and ‘Ce’ multilayers display a similar behavior, not shown; each data point is the average of at least two samples; the data point of the terminal ligand was omitted as it is different for hydroxamate and diphosphonate termination, and therefore cannot be averaged as the
other data points). The CAs of the three single-ion multilayers alternate between ligand-terminated and metal ion-terminated layers, as shown previously for the ‘ZrCl₄’ and ‘Ce’ multilayers, indicating regular growth of the multilayer. The CAs of the mixed ‘ZrCl₄/Ce’ multilayer (not shown) do not show the same degree of regularity. An apparent stabilization of the CA values is seen after about three adsorbed layers (six steps), in agreement with the previously published data for ‘ZrCl₄’ and ‘Ce’ multilayers.⁶

**XPS measurements.** Table 1 shows XPS atomic concentrations measured for all the studied multilayers. The maximal experimental error (estimated from signal-to-noise and reproducibility data) is 5% for C, O, Zr and Au; 15% for P; 10% for Ce; and 25% for N. In Table 2 the data are presented as concentration ratios, together with theoretical values. The latter were calculated based on the model shown schematically in Figure 1B, assuming perfect stoichiometry, the same density of molecules in each layer, and a 1:1 metal ion-to-ligand ratio (empirical formulae used: 1, C₃₀N₄O₈S₂; 2, C₁₇N₄O₁₂; 3, C₁₀P₂O₆). The theoretical values in Table 2 include correction for photoelectron attenuation based on the vertical positions of the layers. Attenuation-corrected atomic concentration ratios were calculated using photoelectron escape length λ = 2.7 nm for layers 1-9 and λ = 3.3 nm for the diphosphonate layer³ and assuming homogeneous vertical distribution of the atoms in each layer. The latter assumption is correct for all atoms except the metal ions, located at the top of each layer, which required an additional attenuation factor to account for the position of the metal ions.

The experimental atomic concentration ratios in Table 2 are relatively close to the attenuation-corrected theoretical values. For the 3-terminated multilayers, where P is located in the top layer, the experimental C/P ratios are smaller, and the C/N ratios are larger, than the respective calculated values. A possible explanation is that the diphosphonate layer is more dense than the tetrahydroxamate layers, thus decreasing the C/P ratio and increasing the C/N ratio. This suggestion may find support in the C/N ratio for the 2-terminated multilayers (Table 2, bottom part), which are closer to the theoretical ones (within experimental error).

The most notable deviation from the calculated (attenuation corrected) atomic ratios in Table 2 is the large excess of Zr in the ‘ZrCl₄’ and ‘ZrCl₄/Ce’ multilayers, by a factor of 5-8 (from C/Zr values; the N/Zr values are less accurate). This excess Zr is accompanied by an excess of O. Assuming that in this case the multilayer is composed of a stoichiometric 1(Zr⁴⁺/2)₄ structure and an oxide phase ZrOₓ, the composition of the latter can be revealed by solving the elemental mass balance equations using the XPS atomic concentrations. For ‘ZrCl₄’ multilayers, the calculated stoichiometric ratio between the Zr and O in the ZrOₓ phase is 1:2.2, suggesting the formation of a ZrO₂ phase between the organic layers. On the other hand, the excess of Ce in ‘Ce’ and ‘ZrCl₄/Ce’ multilayers, as well as the excess of Zr in the ‘Zr(AcAc)₄’ multilayer, are much smaller (a factor of 2.2, 1.3, and 1.4, respectively). The excess of O in these samples is accordingly smaller. These results show that the use of Ce⁴⁺, and particularly
Zr(AcAc)$_4$, leads to multilayers with metal ion atomic concentrations rather close to the theoretical values.

The results indicate two clearly distinguishable types of interlayer binding in Zr(IV)-based coordination self-assembly of bishydroxamate systems. Multilayers constructed using Zr(AcAc)$_4$ are close in Zr atomic concentration to the calculated value, and are therefore assumed to represent systems based on simple metal-organic coordination binding between the layers, i.e. near-stoichiometric $1/(Zr^{4+}/2)_n$ multilayers. This fulfills our objective to find preparation conditions leading to multilayers showing atomic ratios close to those predicted by the basic coordination model, i.e., a 1:1 metal ion-to-ligand ratio.

On the other hand, multilayers constructed using ZrCl$_4$ show a large excess of the metal ion, accompanied by an excess of oxygen, indicating an interlayer binding that deviates considerably from simple metal-organic coordination. It suggests an intriguing composite structure with a zirconia-type phase between the organic layers. The ceramic phase is evenly distributed between the organic layers in the multilayer and is similar in each additional layer. The latter is evident from the angle-resolved XPS results shown in Table 3, where the C/Zr ratio is practically constant at different takeoff angles, indicating homogeneous distribution of the excess Zr(IV) in the vertical direction. This is also consistent with the ellipsometric data (Figure 2), showing a regular multilayer growth, with a larger slope, for the ‘ZrCl$_4$’ multilayer. The large slope may reflect a greater thickness (see below) as well as a larger refractive index ($n=2.2$ for zirconia and 1.45 for the organic layers).

The distinction between the stoichiometric (‘Zr(AcAc)$_4$’) and composite (‘ZrCl$_4$’) multilayers is evident when long-time Zr$^{4+}$ binding experiments are carried out, as shown in Figure 4. An Au substrate with a monolayer of the bishydroxamate disulfide anchor 1 was dipped in binding solutions of ZrCl$_4$ and Zr(AcAc)$_4$, and the ellipsometric $\Delta$ recorded as a function of immersion time. The results show a striking difference: While $\delta\Delta$ stabilizes after ca. 10 min in Zr(AcAc)$_4$ solution, a steady increase in $-\Delta\Delta$ is observed in ZrCl$_4$ solution, not reaching a limit after 4 h (the thickness after 4 h is ca. 3.4 nm, calculated assuming a ZrO$_2$ refractive index of $n=2.2$). This provides additional support to our assumption that the ‘Zr(AcAc)$_4$’ multilayers conform to the simple coordination self-assembly scheme.

Another evidence for the formation of zirconia-type interlayers during multilayer construction in ZrCl$_4$ is obtained by identifying the phase deposited during the long-term exposure of a hydroxamate-terminated surface to ZrCl$_4$ solution (as in Figure 4) using HRTEM imaging. Images of a sample prepared by 3 h dipping in ZrCl$_4$ (see Figure 4), show an amorphous phase on the Au lattice (not shown), in which occasional nanocrystalline domains (2-3 nm in lateral dimension) are seen. The characteristic d-spacing in the nanocrystalline domains is 0.264 nm (Figure 5A), matching the PDF reference value of 0.2635 nm for (002) t-ZrO$_2$ (tetragonal form). This phase is therefore assumed to be amorphous zirconia with occasional nano-domains of
crystalline ZrO₂. Note that literature reports on spontaneous deposition of thin zirconia films on self-assembled, sulfonate-terminated organic monolayers in aqueous solutions indicate the formation of either amorphous\textsuperscript{39,40} or a mixture of nanocrystalline t-ZrO₂ and an amorphous basic zirconium sulfate;\textsuperscript{32,41} the amorphous phase transforms to t-ZrO₂ upon annealing.\textsuperscript{39,42}

**Electrical, structural and mechanical properties.** The multilayers (diphosphonate terminated) were analyzed by the XPS controlled surface charging (CSC) method.\textsuperscript{7} The overall potential drop $V_0$ developed across the overlayer upon turning the flood gun on is proportional to the multilayer electrical resistivity. $V_0$ was determined from the shift of either the P or the Zr signal, as described previously.\textsuperscript{7} The experimental error in $V_0$ is estimated to be 20\%, mostly due to long-term instability of the multilayer under the beam. The relative $V_0$ values for the different multilayers were independent of the specific flood gun settings chosen (see Experimental).

The relative values of $V_0$ (at two different flood gun conditions) for the ‘Zr(AcAc)$_4$', ‘Ce’, ‘ZrCl$_4$’, and ‘ZrCl$_4$/Ce’ multilayers were 1 : 1.3 : 4.0 : 3.7, respectively. These data indicate a much greater electrical resistivity of the composite ‘ZrCl$_4$’ and ‘ZrCl$_4$/Ce’ multilayers compared to the more stoichiometric ‘Zr(AcAc)$_4$’ and ‘Ce’ ones. The relative $V_0$ values for the ‘ZrCl$_4$’ and ‘Ce’ multilayers are in agreement with previously published data.\textsuperscript{7} The results suggest that the inclusion of a zirconia-type phase in the organic multilayers, thus forming a composite structure, improves substantially their dielectric properties.

The morphology of the multilayers was examined by semi-contact AFM imaging, as shown in Figure 6. The different multilayers exhibit morphologies with only minor differences, all being very different from the bare Au, in that the multilayer structure comprises much smaller domains than the Au grains.\textsuperscript{43} Distinct differences appear in the AFM-measured roughness, as shown in Figure 7. The roughness of the ‘ZrCl$_4$’ multilayer is the highest, while that of the ‘Zr(AcAc)$_4$’ multilayer is the lowest,\textsuperscript{44} reflecting the effect of the zirconia-type interlayers on the multilayer morphology.

The multilayers were also subjected to mechanical abrasion using multiple scanning in contact mode at increasing force applied to the AFM tip, to form a ‘window’ in the multilayer (i.e., a defined section of removed multilayer).\textsuperscript{45} All the layers were removed by repetitive scanning down to the gold substrate, indicated by the appearance of the Au morphology (as in Figure 6A) in the ‘window’, exemplified in Figure 8 for a ‘ZrCl$_4$’ multilayer. Multilayer thicknesses were measured as the ‘window’ depth, giving the following values (each value is an average of several ‘windows’): ‘Zr(AcAc)$_4$’, 1.4; ‘Ce’, 1.5; ‘ZrCl$_4$’, 2.4; ‘ZrCl$_4$/Ce’, 2.2. The thickness of the multilayers is therefore strongly influenced by the presence of a zirconia-type nanophase, seen as a substantial thickness gain in the composite multilayers.

The mechanical properties of the multilayers are particularly interesting, specifically the question of whether the composite multilayers show improved stiffness, a common feature of composite materials. To address this point, samples were scanned in contact
mode and the threshold force required to cause irreversible damage was measured. For ‘Zr(AcAc)$_4$’ and ‘Ce’ multilayers, this threshold force was lowest (10 nN and 13 nN, respectively). For ‘ZrCl$_4$’ multilayer, 30 nN was required, however the ‘ZrCl$_4$/Ce’ multilayer remained intact under those conditions. The latter observation is supported by the AFM ‘window’ formation experiments, where the contact force necessary to remove the mixed multilayer was higher than that for all other samples. These results emphasize again the effect of the composite organic-ceramic multilayer structure, adding substantial mechanical stability. The superior stiffness of the mixed multilayer is intriguing and requires further study.

**Conclusions**

It is shown that coordination self-assembly, using the same organic ligand building blocks, can lead to different kinds of multilayers, depending on the metal ion used and the ion binding conditions. In the case of bishydroxamate-based coordination multilayers, use of Zr(AcAc)$_4$ solution (and to a lesser extent, Ce$^{4+}$) in the ion binding step promotes the formation of near-stoichiometric multilayers, conforming to the basic scheme of coordination self-assembly and the expected multilayer structure. A completely different situation is encountered when using a ZrCl$_4$ solution in the ion binding step, in which case the results suggest regular growth of organic-ceramic composite multilayers containing a zirconia-type nanophase, evenly distributed between the organic layers. The latter is established by the ca. 1:2 stoichiometric ratio between Zr and O in the oxide phase, as calculated from XPS elemental analysis of composite multilayers, as well as long-term binding experiments showing deposition of a ZrO$_2$ phase.

LbL self-assembly of organic-ceramic composite multilayers opens the way to the synthesis of nanometer-scale materials with special characteristics. As shown here, the properties of the composite multilayers are markedly different from those of the stoichiometric ones, showing a larger thickness, increased roughness, higher electrical resistivity, and improved stiffness. As the LbL construction scheme in coordination self-assembly is flexible and well controlled, variation of the ion binding conditions is expected to provide effective tuning of the compositional, structural, mechanical, electrical and optical properties of the resulting nanostructures.

**ACKNOWLEDGMENT**

This work was supported by research grants from the Israel Science Foundation and Mr. Ilan Gluzman. A.V. is partially supported by a KAMEA Fellowship, Israel Ministry of Immigrant Absorption. We thank R. Lazar for the synthesis of molecules 1 and 2.
References


(37) HRTEM images of samples prepared by 10 min dipping in ZrCl₄ or Zr(AcAc)₄ showed no features other than the gold lattice.
(38) Figure 5B shows an image of the Au lattice on the same sample, as a reference; d-spacings: 0.239 nm (111) (marked); 0.147 nm (220); 0.124 nm (311); respective PDF reference values: 0.2355 nm; 0.1442 nm; 0.1230 nm.
(43) The multilayer domains in Figure 6 (ca. 10 to 25 nm in diameter) are smaller than the average domain size of 70 nm reported previously. This difference is assumed to arise from the better imaging conditions and decreased tip convolution in the present work.
(44) The difference in roughness is evident from the first coordinated layer (i.e., Au/1/Au⁺) as seen by AFM imaging. See Doron-Mor I., Ph.D. Dissertation, Weizmann Institute of Science, 2004.
(45) Contact mode AFM was used to form the ‘window’, while semi-contact mode was used to image the multilayer before and after ‘window’ formation.
Figure captions

Figure 1. Schematic presentation of the molecules used for multilayer construction (A) and an idealized structure of the coordination-based multilayers (B).

Figure 2. Changes in the ellipsometric parameter Δ vs. number of organic layers during coordination self-assembly of $1/(x^{+}/2)_n$ multilayers on Au (x represents a metal ion).

Figure 3. Variation of water contact angles (CAs) during coordination self-assembly of a ‘Zr(AcAc)$_4$’ multilayer on Au (full circles: advancing CAs; open circles: receding CAs).

Figure 4. Changes in the ellipsometric parameter Δ vs. time of immersion of a monolayer of 1 on Au in solutions of ZrCl$_4$ (circles) and Zr(AcAc)$_4$ (squares).

Figure 5. HRTEM images taken after 3 h immersion of a monolayer of 1 on Au in a solution of ZrCl$_4$ (as in Figure 4), showing (A) a nanocrystalline t-ZrO$_2$ domain on Au, and (B) the Au lattice.

Figure 6. Semi-contact AFM images (500x500 nm$^2$) of $1/(x^{+}/2)_n$ multilayers (n=11 for the ‘ZrAcAc’ multilayer and 9 for all other multilayers) (x represents a metal ion). Z-scale: A – 11 nm, B – 16 nm, C – 12 nm, D – 15 nm, E – 13 nm.

Figure 7. Average roughness of $1/(x^{4+}/2)_n$ multilayers (n=11 for ‘ZrAcAc’ multilayer and 9 for all other multilayers) derived from the AFM images in Figure 6 (x represents a metal ion).

Figure 8. Semi-contact AFM image (1000x1000 nm$^2$) and cross-section of a $1/(Zr^{4+}/2)_9$ multilayer on Au, prepared using ZrCl$_4$; the ‘window’ was created by multiple scanning at increasing force applied to the AFM tip, operated in the contact mode.
Table 1. Atomic concentration % from XPS measurements of the multilayers ($x^+$ represents a metal ion).

<table>
<thead>
<tr>
<th>Multilayer</th>
<th>Procedure</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Zr</th>
<th>Ce</th>
<th>P</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/($x^+$/2)$_6$/x$^+$/3</td>
<td>'ZrCl$_4$'</td>
<td>38.6</td>
<td>43.5</td>
<td>3.5</td>
<td>9.94</td>
<td>4.3</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>'Ce'</td>
<td>45.3</td>
<td>34.1</td>
<td>5.2</td>
<td>5.5</td>
<td>4.0</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>'ZrCl$_4$/Ce'</td>
<td>38.5</td>
<td>43.9</td>
<td>3.7</td>
<td>8.3</td>
<td>0.83</td>
<td>4.0</td>
<td>0.77</td>
</tr>
<tr>
<td>1/($x^+$/2)$_{16}$/x$^+$/3</td>
<td>'Zr(AcAc)$_4$'</td>
<td>45.8</td>
<td>32.6</td>
<td>4.0</td>
<td>3.5</td>
<td>4.3</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>1/($x^+$/2)$_9$</td>
<td>'ZrCl$_4$'</td>
<td>39.5</td>
<td>44.1</td>
<td>7.2</td>
<td>9.0</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>'Ce'</td>
<td>47.2</td>
<td>35.5</td>
<td>8.2</td>
<td>4.4</td>
<td>4.7</td>
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</table>
Table 2. Calculated and experimental atomic concentration ratios from XPS measurements of the multilayers (x represents a metal ion).

<table>
<thead>
<tr>
<th>Multilayer</th>
<th>Procedure</th>
<th>Concentration ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C/N</td>
</tr>
<tr>
<td></td>
<td>Calculated&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Single ion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mixed</td>
</tr>
<tr>
<td>1/(x&lt;sup&gt;-4&lt;/sup&gt;/2)_6/x&lt;sup&gt;-4&lt;/sup&gt;/3</td>
<td>‘ZrCl&lt;sub&gt;4&lt;/sub&gt;’</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>‘Ce’</td>
</tr>
<tr>
<td></td>
<td></td>
<td>‘ZrCl&lt;sub&gt;4&lt;/sub&gt;/Ce’</td>
</tr>
<tr>
<td>1/(x&lt;sup&gt;-4&lt;/sup&gt;/2)_10/x&lt;sup&gt;-4&lt;/sup&gt;/3</td>
<td>‘Zr(AcAc)&lt;sub&gt;4&lt;/sub&gt;’&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.5</td>
</tr>
<tr>
<td>1/(x&lt;sup&gt;-4&lt;/sup&gt;/2)&lt;sub&gt;9&lt;/sub&gt;</td>
<td>Calculated&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>‘ZrCl&lt;sub&gt;4&lt;/sub&gt;’</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>‘Ce’</td>
<td>5.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Corrected for attenuation.

<sup>b</sup> Although the number of layers is different, the theoretical values are practically the same.

Table 3. C/Zr atomic concentration ratio at different takeoff angles in XPS measurements of a ‘ZrCl<sub>4</sub>’ multilayer.

<table>
<thead>
<tr>
<th>Takeoff angle (degrees)</th>
<th>18</th>
<th>25</th>
<th>35</th>
<th>47</th>
<th>62</th>
<th>86</th>
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<tr>
<td>C/Zr</td>
<td>4.3</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5
Figure 7

Figure 8
3.2.1. Scanning probe study of topography changes induced by a coordination monolayer on gold.

The morphological and mechanical differences between the different types of multilayers intrigued us to look for their origin. Thus we attempted to study the morphology of the anchor molecule layer (Fig. 1, 1) and its metal ion complex, using the different metal ion solutions (ZrCl₄, Ce(IV), Zr(AcAc)₆). AFM imaging of the monolayers (either Au/1 or Au/1/metal ion) on 100 nm gold films evaporated on silicon was not successful because of the roughness of the surface (Rₚ=1.45 nm in fig. 2(a)) and the dome shape of the grains. We were unable to see any significant features on the gold grains. Hence, a flat gold surface was needed to reveal the morphological changes effected by self-assembly of one layer. Larger and flatter grains may be obtained by using thermally annealed mica or quartz as substrates for gold evaporation, as can be seen in the STM images of such surfaces (Fig. 2 (b) and (c)).

Although imaging of mono- and bilayers on Au/mica seems possible, it was very difficult and the resolution was low (Fig. 3). This triggered us to find a substrate, which is atomically flat and would provide high-resolution images of the layers. Such substrates are single-crystals Au beads prepared by the method of Clavilier et al.

Large atomically flat facets with (111) orientation are formed on the bead surface which are superior substrates for scanning probe microscopy (Fig. 4). Although more difficult to handle, the gold beads enabled us to study morphological changes of the surface induced by self-assembly of coordination-based mono/bilayers. It may be questioned whether the layers form the same structure on single-crystal gold and grain-structured gold. As shown later, similar features are seen on both surfaces, suggesting that the morphology of the layers is about the same.

![Figure 1. The ligands.](image-url)
Figure 2. STM images (1μm scan) of 100 nm gold evaporated on silicon (a), annealed mica (b) and annealed quartz (c).

Figure 3. AFM image (1μm scan) of 1/Zr⁺ monolayer on 100 nm gold on annealed mica.

Figure 4. Imaging (1 μm scan) of a gold facet by low-current STM (a; z-scale, 5.48 nm) and AAC (Acoustic AC) mode AFM (b; z-scale 7.6 Å). The difference between the z-scale of the images originates from the difference in the number of atomic steps of the gold.
Figure 5 shows an AFM image of a monolayer of the anchor bishydroxamate molecule (1) on a gold bead facet. Gold atomic steps are observed, but no additional features are induced by the monolayer. The roughness of the gold before and after monolayer modification is also of the same order ($R_s = 0.4$ Å for an area of 100x100 nm). However, binding of a metal-ion ($\text{ZrCl}_4$, $\text{Zr}($AcAc$)_4$ or Ce(IV)) changes completely the image. The surface becomes covered with domains, about 10 nm in diameter, for all three metal ion solutions used. AFM image of 1/Zr(IV) complex on a gold facet, prepared using ZrCl$_4$ solution, is also shown in figure 5. The other complexes, i.e. 1/Ce(IV) and 1/Zr(AcAc)$_4$, form the same general structure. Detailed analysis of domain sizes is impossible due to the poor separation between domains, which are either close to each other or seem to be so due to tip convolution.

The roughness is indicative of the structural differences between the samples. It shows that binding of a metal-ion increases the roughness by ca. an order of magnitude. Furthermore, the ‘ZrCl$_4$’ layer is considerably rougher than the other two (Fig. 6). Hence, significant differences are already obtained in the first monolayer.

In the next two steps of multilayer construction, i.e. formation of a coordination bilayer, the overall domain structure (not shown) does not change, yet the roughness increases (Fig. 6). The ‘ZrCl$_4$’ layer remains the roughest, while the ‘Zr(AcAc)$_4$’ and ‘Ce’ layers show a lower roughness with certain fluctuations.

Figure 5. AAC mode AFM image of (a) gold bead/1 (1000 nm scan) and (b) gold bead/1/Zr(IV) (500 nm scan).
Figure 6. Average roughness of multilayers (The layers adsorbed are indicated) on a gold bead. Data taken from AFM images (500x500 nm area) (X represents a metal ion).

It is known that Zr(IV)-tetrahydroxamate complexes decompose in acidic media due to competition between protons and Zr(IV) ions. This was used previously\textsuperscript{7} to chemically manipulate a hybrid multilayer (containing tetrahydroxamate and diphosphonate ligands) by pH changes. Hence it was interesting to see whether the domain structure, dictated by metal-ion binding, would disappear upon exposure of the complex-monolayer to acidic solution. Samples of 1/Zr(IV), using ZrCl\textsubscript{4} and Zr(AcAc)\textsubscript{4}, and a control sample of the anchor molecule (1), were immersed in 1 M HCl overnight. The samples were analyzed by ellipsometry, AFM and XPS. Preliminary results (not shown) indicate that acid treatment of 1/Zr(IV) monolayers on Au cause disappearance of the domain structure, and a reduction in the film roughness and thickness. These results further relate the appearance of a domain structure to binding of Zr\textsuperscript{4+}. 

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Experimental

All the experimental details are found in section 3.2., except for the Au substrate and the scanning probe microscopy.

The Au substrate:

Faceted gold: A gold wire, 1.0 mm in diameter, was scorched in an oxygen-rich butane flame to form a molten bead, which was cooled slowly and crystallized, forming a single-crystal bead.

Evaporated gold: 100 nm Au/mica films were prepared by mounting freshly cleaved mica substrates in a cryo-HV evaporator (Key High Vacuum) equipped with a Maxtek TM-100 thickness monitor. Before Au evaporation, the mica was annealed at about 250°C, under 2x10^{-6} torr, overnight (>12 hrs). Homogeneous deposition was obtained by moderate rotation of the substrate plate. Gold (99.99%) was evaporated from a tungsten boat at 2x10^{-6} torr, 250°C at a deposition rate of 1 Å/sec. The temperature at the end of the evaporation was above 300°C. The samples were annealed for 6h at 300°C under vacuum in the evaporator, and were allowed to cool to room temperature before removal from of the evaporator. Evaporation on quartz was done using the same conditions.

Atomic Force Microscopy (AFM): AFM images were recorded in air using Molecular Imaging PicoScan™ (Pico IC) instrument (except for Fig. 3b which was recorded using a Nanoscope IIIa microscope (Digital Instruments, Inc.)) operated in the Acoustic AC (AAC) mode (tapping mode). The cantilevers used were NSC12 and CSC12 series of ultrasharp silicon (MikroMash, Estonia), with a resonant frequency of (100-200) kHz and an average tip radius of ≤10 nm.

Scanning Tunneling Microscopy (STM): STM images were taken using a Nanoscope IIIa microscope (Digital Instruments, Inc.) operated in the low current STM mode. The tips were prepared as follows: A Pt/Ir wire was electrochemically etched using 1M NaCl solution and applying AC voltage in the range 0-80V. The tips were cleaned with triply distilled water and with abs. ethanol after etching. The tips were checked by optical microscope before using.
References:

3.2.2. Coordination oligomers on Au substrate

The construction scheme of coordination-based self-assembled multilayer\(^1\), which is used throughout this work, enables highly controlled layer-by-layer construction of three-dimensional metal-organic multilayers and superlattices of substantial variability, upon varying the first ligand layer, the coordinated metal-ions or the organic linkers. Yet, the process is time-consuming (ca. one day per layer) and therefore impractical for the construction of a large number of layers. Construction of multilayers may be more practical if more than one monolayer could be assembled in each step, namely, through a pseudo-polymerization process.

Coordination polymers, that is, polymers whose repeat units are held together by coordinative bonds, are of considerable current interest not only in supramolecular science but also because of their potential use as magnetic, electronic or optical materials.\(^2\) They may also be used in crystal engineering and for the construction of novel networks containing inner cavities and channels with controlled size, shape, and chemical environments for applications in separation, catalysis and optoelectronics.\(^3,4\) There are a number of publications on the synthesis of ion coordination polymers in solution for the different applications mentioned above,\(^5-9\) yet, only few studies on the construction of ion coordination polymer on a solid substrate have been published.\(^10-12\)

In this part of my study I present preliminary results on a new method for the construction of organic/metal ion multilayers on gold substrate, via step-by-step assembly of coordination oligomers. The building process was monitored by ellipsometry measurements (the thickness of the multilayers was calculated using \(n_p = 1.45\)).

Preparation of coordination-based ultrathin polymeric films should be achieved, in principle, by a simple two-step procedure: (i) assembly of the first monolayer containing coordination sites for ion binding, same as the first step in the layer-by-layer preparation; (ii) exposure of the monolayer to a solution containing both the 8-coordinating metal ion and the bifunctional organic ligand. This should promote spontaneous growth of a coordination polymer from the surface. Simultaneous polymer growth in solution can be avoided by using low concentrations of the components.

Thus, the possibility of growing linear coordination polymers from the gold surface was tested, starting from a SA monolayer of the disulfide bishydroxamate molecule (the anchor molecule) (Figure 1, 1), followed by a single dipping in a solution
containing both the tetrahydroxamate binder (Figure 1, 2) and a metal ion (Ce\(^{4+}\)). In order to control the polymerization rate and minimize polymer formation in the solution, the concentrations of the tetrahydroxamate and metal ion were kept low (0.3 mM and 0.03 mM, respectively) compared to the concentrations used in the step-by-step assembly of the multilayers (3 mM ligand and 1 mM metal ion).

![Figure 1. The ligands.](image)

The influence of several parameters was checked:

a) Using different solvents for the mixed solution of tetrahydroxamate binder and the metal ion: Solution A – Molecule 2 was dissolved in ethanol. Ce\(^{4+}\) was added from 1 mM (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) in H\(_2\)O (pH 3.3, adjusted with ammonium hydroxide). Solution B - (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) and molecule 2 were dissolved in a buffer solution containing 0.1 N MES (2-[N-Morpholino]ethanesulfonic acid) buffer and ethanol (1:4) (pH adjusted to 6 with ammonium hydroxide). Adsorption from solution A is based on the adsorption conditions used in the step-by-step construction of the multilayers. Solution B (using different concentrations of the binder and metal ion) was previously used for polymerization in solution.\(^{13}\) Both multilayers were grown on a monolayer of the anchor molecule 1.

Figure 2 shows the change of the ellipsometric thickness of the layer vs. the adsorption time for a layer grown in solutions A and B (including the first monolayer). In solution A the growth of the layer stopped after about 3 h and the thickness was about 40 Å, which corresponds to the addition of ca. 2 tetrahydroxamate layers. In solution B after 50 h the thickness of the layer was about 140 Å, which corresponds to the addition of ca. 9 tetrahydroxamate layers. Later measurements in solution B have shown different thickness values (ca. 65 Å after 50 h; see the following experiments). This implies an
unstable nature of the polymerization solution. The difference between solutions A and B may be due to the higher pH in solution B, which shifts the equilibrium to complex formation.

![Graph showing thickness vs. adsorption time](image)

**Figure 2.** Ellipsometric measurements of multilayer construction according to the procedure in (a).

*b) Binding of a Ce⁴⁺ layer to the anchor molecule before dipping in the mixed solution:* Two preparation protocols were compared. In the first, a gold substrate covered with a SA monolayer of the anchor molecule (1) was dipped in solution B. In the second, Ce⁴⁺ was bound to the monolayer of 1 before dipping in solution B. This experiment (Fig. 2) shows that the initial complexation with Ce⁴⁺ gives thickness advantage only in the initial stages. The difference in the thickness is insignificant after about 30 h. The thickness of the multilayers reached about 90 Å (Fig. 3).

![Graph showing thickness vs. time](image)

**Figure 3.** Ellipsometric measurements of multilayer construction according to procedure (b).
c) Using different concentrations of the metal ion in the mixed solution: Gold substrates with an adsorbed SA monolayer of the anchor molecule (1) were dipped in solution B that contained 0.3 mM tetrahydroxamate binder (2) and 0.03, 0.06, 0.09 and 0.12 mM Ce⁴⁺. There was no significant difference in the thickness of the multilayers that were constructed in the different solutions. The thickness of the layers was about 85 Å, which corresponds to ca. 6 layers.

d) Addition of a fixed amount of Ce⁴⁺ to the mixed solution after stabilization of the multilayer thickness: From the results of the previous experiments, it seemed that the growth of the layers after about 24 h gets much slower. A reasonable assumption was that in this period all the Ce⁴⁺ ions that did not bind to surface binders are consumed by the ligands in the solution. Thus, after about 24 h the multilayer on the gold surface grows very slowly, until the growth is stopped. This assumption was substantiated by the following experiments:

i) A SA monolayer of the anchor molecule (1) was adsorbed on a gold substrate. The substrate was dipped in solution B that was prepared at least 12 h before the dipping. There was essentially no growth above the first monolayer even after 45 h (Fig. 4). Addition of 0.03 mM Ce⁴⁺ to the adsorption solution and dipping the substrate immediately after the addition resulted in growth of about 2 tetrahydroxamate layers. Waiting overnight for stabilization of the growth and adding the same amount of Ce⁴⁺ again caused a similar growth in the thickness of the multilayer (Fig. 4).

![Figure 4. Ellipsometric measurements of multilayer construction according to procedure (d-i).](image)

ii) A SA monolayer of the anchor molecule (1) was adsorbed on a gold substrate. The substrate was dipped in solution B immediately after its preparation. After about 24 h...
the growth of the multilayer stopped, and the thickness was about 80 Å (Fig. 5). Addition of 0.03 mM Ce$^{4+}$ to the adsorption solution and dipping two of the substrates (Fig. 5, circles) immediately after the addition resulted in the growth of about 2 tetrahydroxamate (2) layers. Dipping two other substrates (Fig. 5, squares) in the solution without Ce$^{4+}$ addition resulted in no additional growth. The cycle of addition of Ce$^{4+}$ and waiting for stabilization of the growth was repeated several times with similar results (Fig. 5).

![Figure 5. Ellipsometric measurements of multilayer construction according to procedure (d-ii). Each line is the average of two slides.](image)

To conclude, preliminary results with Ce(IV) indicate formation of oligomeric units in the polymerization solution. The results suggest that the solvent and the concentration ratio between the organic ligand and the binding ion may determine the length of the oligomers, and influence the process of layer growth on the substrate. Under the conditions of figures 4 and 5 the dominant species in the solution appears to be a dimer.

**Experimental**

**Chemicals.** Molecules 1, 2 were synthesized as previously reported. Chloroform (Biolab, AR), was passed through a column of activated basic alumina (Alumina B, Akt. 1, ICN). Ethanol (Merck, AR), H$_2$O$_2$ (Merck), NaOH (Merck, AR), HNO$_3$ (Palacid, 69-70%), HCl (Frutarom, 32%), [(NH$_4$)$_2$Ce(NO$_3$)$_6$] (BDH, AR), MES buffer (2-[N-Morpholino]ethanesulfonic acid) were used as received. Water was triply distilled. Gas used was purified house nitrogen.

**Gold electrodes.** Gold films, 100 nm thick, were evaporated onto optically polished n-type single-crystal (111) silicon wafers (Aurel, Landsberg, Germany) as previously described. The gold-covered slides were annealed in air for 3 h at 250°C and left to cool to ambient temperature.
Monolayer Preparation. Monolayers of the anchor disulfide bishydroxamate (1) molecule were prepared as previously described.\textsuperscript{14}

Ellipsometry. A Rudolph Research Auto-EL IV null ellipsometer operating at an angle of incidence of 70° and a wavelength of 632.8 nm was used for ellipsometric measurements according to the previously described procedure.\textsuperscript{15}

References:


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3.2.3. Construction and characterization of hydroxyquinoline-based bilayers and multilayers

Introduction

Coordination-based multilayers provide a versatile supramolecular structure since one can control its properties by changing the ligand and the metal-ion used. We found hydroxyquinoline (HQ) as an attractive candidate for the multilayer construction scheme because of the great interest in HQ complexes in the fabrication of light emitting devices. Among the HQ complexes used as emissive layers in light emitting diodes (OLEDs) are those containing Al(III)$^{1,2}$, Ga(III)$^{3}$, Nd(III)$^{4}$, Er(III)$^{5,6}$ and Yb(III)$^{6}$. A number of factors influence the performance of OLEDs, some of these factors are inherent to the materials themselves and others involve the type of device and its preparation. In particular, it has been shown that the most efficient OLEDs involve heterostructures, which contain separate carrier injection/transport and emissive layers.$^{7}$ Good control of both the uniformity and thickness of these layers is critical in obtaining efficient devices. To achieve this control the method of layer-by-layer assembly of charged polymers$^{8}$ was adopted, forming polymeric light emitting devices.$^{9,10}$

It seems that our construction scheme of coordination-based self-assembly multilayers may provide control at the molecular level on the thickness and organization of hydroxyquinoline-based multilayer, which may be used as emissive layers. It has been shown previously$^{12}$ that the fluorescence properties of Zr(IV) tetrahydroxyquinoline complexes (in solution) resemble those of Al(III), making them a convenient ligand for multilayer construction.

In the present study, an anchor molecule (Fig. 1 (a), 4), containing two hydroxyquinoline groups and a disulfide residue, was designed and synthesized.$^{13}$ We succeeded in forming bilayers on gold (100 nm Au evaporated on silicon) by either of two processes: i) a one-step process, using the preformed 2:1 complex (7); ii) a stepwise process involving formation of the anchor monolayer followed by successive binding of the guest ions and a second monolayer of the same molecules (Fig. 1 (b)). The one step approach allows the construction of symmetric bilayers, while providing the possibility of full characterization of the 2:1 complex prior to bilayer assembly; this is useful in substantiating the bilayer composition. The step-by-step procedure has the advantage of enabling construction of asymmetric (as well as symmetric) bilayers and, with appropriate ligands, multilayer formation. Both processes were monitored by
ellipsometry, contact angle, ac impedance and XPS measurements. The step-by-step construction was carried out also on gold island film, which enabled us to monitor the process by T-SPR spectroscopy. In addition, we have preliminary results on the preparation of a bilayer with aluminum, which is a 6-coordination metal-ion. Thus, molecule 5 (Fig. 1) was used as the second layer to form the bilayer (4/Al(III)/5).

Another ligand, containing four hydroxyquinoline groups (Fig. 1 (a), 6), was designed and synthesized, to enable the construction of a multilayer. We succeeded in forming the asymmetric bilayer 4/Zr(IV)/6 (monitored by ellipsometric, CAs and XPS measurements) and have some preliminary results on the formation of a multilayer (6 layers) base on molecule 6.

Figure 1. (a) The studied molecules. (b) Formation of symmetric bilayers on gold surface using either preformed complex (right) or a stepwise procedure (left).

Experimental

Chemicals: Molecules 4, 5 and 6 were synthesized by David Margulies of Prof. A. Shanzer’s group. Zirconium acetylacetonate (Zr(AcAc)₄) (Fluka, purum) and aluminum acetylacetonate (Al(AcAc)₃) (Aldrich, 99%) were used without further purification. Chloroform (Biolab, AR) was passed through a column of activated basic alumina. Ethanol (Merck, AR), 2,2,2-trifluoroethanol (TFE) (Sigma, 99%), H₂O₂ (Merck, 30%).
NaOH (Merck, AR), HNO₃ (Palacid, 69-70%) were used as received. Water was triply distilled. The gas used was purified house nitrogen (from liquid N₂).

**Gold electrodes:** Gold films, 100 nm thick, were evaporated onto optically polished n-type single-crystal (111) silicon wafers (Aurel, Landsberg, Germany) as previously described. The gold-covered slides were annealed in air for 3 h at 250°C and left to cool to ambient temperature. Gold island films, 2.5 nm (nominal thickness), were evaporated on 3-mercaptopropyl trimethoxysilane (MPTS) - modified glass as described in section 3.3.

**Monolayer preparation:** The gold substrates were pretreated with UV/ozone by means of a UVOCs instrument, then immersed in ethanol for 20 min and dried under a stream of N₂. A monolayer was adsorbed by immersion of the gold substrate in 3 mM solution of 4 in TFE overnight. The slides were rinsed with TFE and ethanol, then immersed in ethanol for 20 min and dried under a stream of N₂.

**Preparation of preformed bilayers:** A preformed bilayer was assembled by the procedure described above for the monolayer.

**Step-by-step preparation of bilayers and multilayers:** Following monolayer preparation (as above), the slides were immersed in 1 mM TFE solution of Zr(AcAc)₄ or Al(AcAc)₃ overnight, then rinsed with TFE and ethanol, immersed in ethanol for 10 min and dried under a stream of N₂. For construction of the second organic layer, the slides were immersed in a 3 mM solution of 4, 5 or 6 in TFE overnight. The slide were then rinsed with TFE and ethanol and dried under a stream of N₂. Multilayers were assembled by alternate adsorption of an ion-binding layers and tetrahydroxyquinoline ligand layers.

**Ellipsometry:** A Rudolph Research Auto-EL IV null ellipsometer operating at an angle of incidence of 70° and a wavelength of 632.8 nm was used for ellipsometric measurements, according to a previously described procedure.

**Contact Angle (CA) measurements:** Water CAAs (advancing and receding) were measured within 10 min after adsorption. Three measurements at different spots were carried out. The accuracy of the measurement is ±2°. A Rame-Hart NRL Model 100 contact angle goniometer was used.

**AC-impedance spectroscopy** is an electrochemical method, which is based upon the measurement of the response of an electrochemical system to a small amplitude sinusoidal voltage perturbation, varied in a wide frequency range. The response is often
analyzed using the complex-impedance presentation, i.e. the real vs. imaginary components of the impedance at different frequencies, and the results are interpreted in terms of an equivalent electrical circuit. AC-impedance measurement using Fe(CN)

³/Fe(CN)

⁶ were carried out as previously described.

X-ray photoelectron spectroscopy (XPS): XPS measurements were carried out with Kratos Axis HS XPS system, using monochromatized Al(Kα) X-ray source (hv = 1486.6 eV).

UV-vis spectroscopy (T-SPR): see sections 3.3. and 3.4.

Results and discussion

Design and synthesis: Figure 2 illustrates the synthetic steps for the preparation of the three molecules, designed as building blocks for the construction of fluorescent multilayers on gold surfaces. Compounds 4, 5 and 6 incorporate in their skeleton hydroxyquinoline (8-HQ) ligands, which can efficiently bind to zirconium(IV) or aluminum(III) ions and form fluorescent metal complexes. Molecule 4, which serves as an anchoring group to gold surfaces, contains a disulfide five-membered ring with two extending chains terminated with 8-HQ ligands. The dithiolane ring group serves as immobilization group, which decreases the degree of freedom in the molecule, and the extending chains form a defined cavity for metal ion binding. Molecule 5 is a simple 8-HQ derivative and is utilized to bind 6-coordinating Al(III) ions. Molecule 6 functions as a coordination extension unit. It contains four 8-HQ ligands, and can bind to 8-coordinating zirconium ion in the previous layer with only two of its 8-HQ binding groups. To the other two, a second zirconium ion can complex in such a way that a stepwise construction of the layers is established, and a multilayer structure is achieved.

The final compounds were purified by HPLC and identified by the following spectroscopic techniques: NMR, IR, UV-Vis and fluorescence spectra. Titration of 4 with aluminum acetyl acetonate, followed by measuring the absorption in solution revealed a 1:1 ratio between 4 and Al (III), whereas, titration with zirconium acetylacetonate indicated 2:1 ratio, which was further verified by electron spray mass spectroscopy.
Figure 2. Preparation scheme of molecules 4, 5, 6.

Preformed bilayer assembly: In a one-step process, symmetric bilayer of 4 with Zr(IV) was assembled by immersion of gold substrate in a solution of the preformed complex 7 (Fig. 1 (a)) and characterized by ellipsometry, contact angle (CA) measurements, XPS and AC-impedance spectroscopy (Table 1). A thickness of 30-32 Å (for n = 1.45) was determined ellipsometrically for the bilayer, which is similar to the theoretical thickness (31-33 Å), calculated from a model assuming of perpendicular orientation. The low CA hysteresis (2°) implies good order of the system.

The chemical composition of the preformed bilayer was determined by XPS measurements (Table 1). The experimental error for the carbon, oxygen, zirconium and Au was usually less than five percent (the error was estimated by the S/N and by the reproducibility of the measurements). The experimental error for the sulfur and nitrogen was up to 10%. Table 2 shows the experimental atomic concentration ratios compared to those calculated by stoichiometry. The differences between the values for the various elements implies the presence of impurities of the asymmetric complex 4/Zr(AcAc)₂ (the complexation is done with Zr(AcAc)₄). In this complex the amount of carbon and nitrogen in the upper layer is lower than that in the preformed complex 4/Zr/4. The sulfur atoms in the impurity 4/Zr(AcAc)₂ are located in the innermost part of the layer, therefore, in the presence of the impurities the intensity of the sulfur is decreased. An excess of oxygen is also observed, which might be due to air contaminants and water
molecules incorporated in the layer. The extent of surface coverage determined by ac-
impedance spectroscopy\textsuperscript{21} is rather high (95%).

\textit{Stepwise bilayer assembly:} Symmetric bilayers of 4 with Zr(IV) were also formed
by a step-by-step process. Bilayer formation involves i) adsorption of the disulfide
bishydroxyquinoline (4) on Au to obtain a ligand monolayer (ellipsometric thickness
18-21 Å for \( n_r = 1.45 \); surface coverage: 98%; CAs: adv 59°, rec 55°); ii) exposure of the
monolayer to Zr(\textit{AcAc})\textsubscript{4} solution (1mM in TFE) followed by a rinse with TFE and
EtOH to provide the respective monolayer complex (ellipsometric thickness 21-25 Å for
\( n_r = 1.45 \); CAs: adv 55°, rec 48°) and iii) exposure of the monolayer complex to solution
of 4 to obtain the symmetric bilayer.

Characterization of the bilayer is summarized in table 1. The ellipsometry and CA
values are quite similar to the one-step process. The slight difference in the coverage is
within the experimental error. The C/S and C/Zr atomic concentration ratios (Table 2),
derived from XPS measurements, are closer to the stoichiometric ones, suggesting that
exchange of the acetylaceionate with the HQ ligand on the surface is more efficient. An
excess of oxygen is observed here also. To conclude, the similarity in the properties of
bilayers prepared by the two methods provides confidence in the structure of these
assemblies.

<table>
<thead>
<tr>
<th>Bilayer</th>
<th>Theoretical perpendicular thickness (Å)</th>
<th>Ellipsometric thickness (Å)</th>
<th>Adv CA (H\textsubscript{2}O)</th>
<th>Rec CA (H\textsubscript{2}O)</th>
<th>% Coverage</th>
<th>XPS results (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au</td>
</tr>
<tr>
<td>4/Zr(IV)/4 preformed</td>
<td>31-33</td>
<td>30-32</td>
<td>52</td>
<td>49</td>
<td>95</td>
<td>33.2</td>
</tr>
<tr>
<td>4/Zr(IV)/4 step-by-step</td>
<td>31-33</td>
<td>29-32</td>
<td>53</td>
<td>52</td>
<td>99</td>
<td>30.6</td>
</tr>
<tr>
<td>4/Zr(IV)/6</td>
<td>---------</td>
<td>24-27</td>
<td>52</td>
<td>46</td>
<td>100</td>
<td>32.2</td>
</tr>
</tbody>
</table>

\textbf{Table 1.} Characterization of HQ bilayers.

<table>
<thead>
<tr>
<th>Bilayer</th>
<th>C/N</th>
<th>C/O</th>
<th>C/S</th>
<th>C/Zr</th>
<th>N/Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/Zr(IV)/4</td>
<td>5.8</td>
<td>4.4</td>
<td>17.5</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>Experimental- preformed</td>
<td>5.0</td>
<td>2.7</td>
<td>25.6</td>
<td>48</td>
<td>9.5</td>
</tr>
<tr>
<td>Experimental - step-by-step</td>
<td>7.7</td>
<td>2.5</td>
<td>13.9</td>
<td>67</td>
<td>8.75</td>
</tr>
<tr>
<td>4/Zr(IV)/6</td>
<td>5.6</td>
<td>4.2</td>
<td>50</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>Experimental</td>
<td>8.4</td>
<td>3.0</td>
<td>25</td>
<td>85</td>
<td>10</td>
</tr>
</tbody>
</table>

\textbf{Table 2.} Experimental (XPS measurements) and stoichiometric atomic concentration ratios
Stepwise bilayer assembly on gold island films: Stepwise formation of the symmetric Zr(IV) bilayer was also followed by T-SPR spectroscopy (see section 3.4).\textsuperscript{14,15,22} The step-by-step construction scheme was applied on 2.5 nm (nominal thickness) Au island film evaporated on MPTS modified glass (see section 3.3 and 3.4).\textsuperscript{14,17} After each added layer the sample was rinsed and dried and a transmission UV/Vis spectrum was taken in air. An increase of the extinction and a red shift of the maximum of the surface plasmon band were observed upon addition of each layer (Fig. 3). This trend is similar to that observed for the hydroxamate-based molecules (section 3.4); however, the plasmon intensity change (PIC)\textsuperscript{14,15,22} is higher for the HQ molecule. These preliminary results also demonstrate the possibility of obtaining quantitative information on mono/multilayer construction from T-SPR spectroscopy.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{Sequential transmission UV/Vis (T-SPR) spectra of 2.5 nm gold island films (unannealed) taken after construction of each layer in the bilayer. Dashed lines correspond to the bare gold.}
\end{figure}

Multilayer construction: In order to form coordination multilayers based on hydroxyquinoline ligands, a tetrahydroxyquinoline binder (Fig. 1a, 6) was synthesized\textsuperscript{13}. As a first step an asymmetric bilayer containing the anchor ligand 4 as the base layer, Zr(IV) as the binding ion and 6 as the second layer, was constructed and monitored by ellipsometry and XPS. The results, summarized in table 1, are as follows: 1) the additional thickness effected by the layer of 6 is low (4-7Å); 2) the atomic concentration ratios measured by XPS compared to the stoichiometric ones (Table 2) for the bilayer 4/Zr(IV)/6 shows that there is a reduced amount of nitrogen and an excess of sulfur (which should be even lower than the stoichiometric one due to attenuation). Both
XPS and ellipsometry results may indicate that molecule 6 did not bind to all the available Zr(IV) sites. The extra oxygen found might be due to air contaminants and water molecules incorporated in the layer. Although it seems that molecule 6 does not bind to all the Zr(IV) sites, continuing the construction of a multilayer results in a regular thickness increase, as seen by ellipsometry (Fig. 4 (a)). Inspection of the CAs vs. the number of layers of HQ (Fig. 4 (b)) compared to the CAs of the hydroxamate multilayer (section 3.2.)\textsuperscript{23,24} reveals the beginning of stabilization of the CAs after the 4\textsuperscript{th} organic layer.

\textbf{Figure 4.} Changes of the thickness (a), calculated from the ellipsometric parameter $\Delta$, and CAs (b) with the number of organic layers in the construction of a 4/(Zr$^{4+}$/6)\textsubscript{3} multilayer on gold. In (b) the CAs of the Zr$^{4+}$ ion coordination are also indicated.

\textit{Hydroxyquinoline complexation with Al(III):} As mentioned above, Al(III)-hydroxyquinoline is used for OLEDs. Thus, there is an interest in constructing multilayer with six coordinated aluminum ions. The complexation of excess of the model ligand (Fig. 1 (a), 5) with Al(AcAc)$_{3}$ in CHCl$_{3}$ was successful and yielded complex 8 (Fig. 5), which was characterized by ES-MS\textsuperscript{13}. Thus, this molecule was used as a model for bilayer formation of HQ ligand with aluminum.

\textbf{Figure 5:} Complex of 8-hydroxyquinoline and aluminum (8).
Figure 6 describes the construction of aluminum-based bilayers, using the model molecule 5. It involves: (i) Adsorption of a monolayer of di-8-HQ derivative (4) on gold. (ii) Exposure of the monolayer to a solution of Al(AcAc)$_2$ in TFE, yielding the respective monolayer complex. (iii) Exposure of the monolayer complex to solutions of ligand 5 to obtain the bilayers 4/Al(III)/5.

Preliminary results on the properties of the bilayer are summarized in table 3. The ellipsometric thickness of 4/Al(III)/5 (24-26 Å, for $n_r = 1.45$) is close to the theoretical perpendicular thickness (27-30 Å). XPS measurements revealed the presence of aluminum in the layers. However, the aluminum signal is low and it suffers from a strong background of the gold signal, which increases the experimental error to 40%. Table 4 shows the concentration ratios of the elements compared to the stoichiometric ones. It can be seen that there is excess of both oxygen and carbon compared to the nitrogen, which might be due to air contaminants (water, hydrocarbons etc.). The ratio N/Al is similar (within the experimental error) to the stoichiometric ratio.

To conclude, synthesis of a ligand comprising three "arms" with HQ moieties will be optimal for the construction of an Al(III) based multilayer. Another option is to use a ligand with two HQ "arms" and the tetrahydroxyquinoline 5 alternatingly.

**Table 3.** Characterization of a 4/Al(III)/5 bilayer.

<table>
<thead>
<tr>
<th>bilayer</th>
<th>Theoretical perpendicular thickness (Å)</th>
<th>Ellipsometric thickness (Å)</th>
<th>% Coverage</th>
<th>XPS results (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/Al(III)/5</td>
<td>27-30</td>
<td>24-26</td>
<td>98</td>
<td>Au 13.5  S 2.3  C 59.1  O 17.3  N 7.14  Al 0.66</td>
</tr>
</tbody>
</table>

**Table 4.** Stoichiometric and experimental (XPS measurements) atomic concentration ratios.

<table>
<thead>
<tr>
<th></th>
<th>C/N</th>
<th>C/O</th>
<th>C/S</th>
<th>C/Al</th>
<th>N/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/Al(III)/5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichiometric ratio</td>
<td>5.8</td>
<td>4.3</td>
<td>26</td>
<td>52</td>
<td>9</td>
</tr>
<tr>
<td>Experimental</td>
<td>8.3</td>
<td>3.4</td>
<td>26</td>
<td>90</td>
<td>10.8</td>
</tr>
</tbody>
</table>
Figure 6. A schematic illustration of construction of bilayer, based on hydroxyquinoline ligands with Al(III).

References

(9) Decher, G. Science 1997, 277, 1232-1237; and refs. therein.
(13) Molecules 4, 5, 6, the Zr(IV) preformed complex of 4 (7) and the complex 8 were designed, synthesized and characterized by D. Margulies of Prof. A. Shanzel's group.

(14) Doron-Mor, I.; Cohen, H.; Barkay, Z.; Shanzel, A.; Vaskevich, A.; Rubinstein, I. Submitted.


(17) Doron-Mor, I.; Barkay, Z.; Filip-Granit, N.; Vaskevich, A.; Rubinstein, I. Accepted to Chem. Mater.


3.3. Ultrathin Gold Island Films on Silanized Glass. Morphology and Optical Properties

I. Doron-Mor, Z. Barkay, N. Filip-Granit, A. Vaskevich and I. Rubinstein

*Accepted to Chem. Mater.*
Ultrathin Gold Island Films on Silanized Glass. Morphology and Optical Properties

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RECEIVED DATE

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Evaporated gold island films have been the subject of studies dealing with a variety of spectrophotometric and sensing applications. Development of these and other applications requires film stability as well as tunability of the morphology and optical properties of the island films. In the present work ultrathin, island-type gold films were prepared by evaporation of 1.0 to 15.0 nm (nominal thickness) gold at a rate of 0.005-0.01 nm s\(^{-1}\) onto glass substrates modified with 3-mercaptopropyl trimethoxysilane (MPTS), the latter used to improve the Au adhesion to the glass. The morphology of the films, either unannealed or annealed (20 h at 200°C), was studied using atomic force microscopy (AFM) and high-resolution scanning electron microscopy (HR-SEM). The information provided by the two imaging techniques is complementary, giving a good estimate of the shape of the islands and its variation with film thickness and annealing. The optical properties of the films were examined using transmission UV/Vis spectroscopy, showing a strong dependence of the localized Au surface plasmon (SP) band on the morphology of the island films. The imaging and spectroscopy indicate a gradual transition from isolated islands to a continuous film upon increasing the Au thickness.

Keywords: Gold, islands, morphology, T-SPR, spectroscopy, AFM, SEM, sensors.
Introduction

Discontinuous evaporated gold films have been used in various applications, including sensing based on transmission surface plasmon resonance (T-SPR) spectroscopy,\(^1\)-\(^3\) surface-enhanced Raman spectroscopy (SERS),\(^4\)-\(^10\) and infrared spectroscopy.\(^11\)-\(^16\) The morphology of such films has been studied previously.\(^17\) Ultrathin (ca., 1-10 nm) island-type films of noble metals (Au, Ag, Cu) evaporated on transparent substrates exhibit transmission spectra showing an absorption band attributed to localized surface plasmon (SP) excitation, similar to systems consisting of dispersed metal particles.\(^18\) The localized SP absorption characteristic of such films is highly sensitive to the dielectric constant of the surrounding medium,\(^19\)-\(^22\) hence changes in the immediate environment of the island surface can be monitored by changes in the SP absorption band, using transmission UV/Vis spectroscopy. The optical response is sensitive enough to monitor adsorption of molecules on the metal island surface down to (sub)monolayer coverage,\(^1\),\(^23\) follow changes in the chain length of alkanethiol self-assembled monolayers\(^24\) or the concentration of analytes in solution.\(^25\) The method was termed transmission surface plasmon resonance (T-SPR) spectroscopy, and its usefulness in various sensing application, in gas or liquid phase, was demonstrated.\(^2\) Biological applications of T-SPR spectroscopy in detecting DNA hybridization\(^26\) and in specific protein recognition\(^3\) appear promising for biosensing.

Ag and Au island films have been widely used in surface-enhanced Raman spectroscopy (SERS) and infra-red spectroscopy, based on the local increase of the electromagnetic field near the surface of metal islands.\(^13\),\(^27\) Despite extensive efforts during more than two decades, reliable platforms for high-sensitivity output in both methods are still being sought, with emphasis on optimization of the film morphology.\(^4\),\(^8\),\(^9\),\(^28\)

In the present work glass slides served as substrates for Au evaporation, offering a smooth, transparent, chemically inert, and inexpensive platform, yet known to exhibit poor adhesion to noble metals. Hence, Au island films evaporated on bare glass show poor stability in various solvents, including water.\(^5\) A similar problem was encountered with Ag island films on glass.\(^29\) Improvement of the adhesion is commonly achieved by evaporation of a 5-10 nm Cr, Ni, or Ti underlayer.\(^30\) However, strong damping of the SERS signal was found for Au island films evaporated on a metal underlayer,\(^5\) and the absorbance of the metal (oxide) adhesion layer would impose additional requirements on the optical instrumentation. A viable possibility for improvement of evaporated metal adhesion is precoating the glass substrate with a self-assembled layer of a mercapto- or amino-silane.\(^5\),\(^31\)-\(^33\) The glass substrates used in the present work were therefore pretreated with 3-mercaptopropyl trimethoxysilane (MPTS) to improve the adhesion of the Au to the glass.\(^31\)

The morphology and optical properties of Au island films on several substrates have been studied previously. The structure and absorbance of Au island films evaporated on
bare mica and quartz were reported\textsuperscript{1,2,23} in the context of the development of T-SPR spectroscopy. However, Au island films grown on an adhesive substrate, i.e., on glass precoated with a silane adhesion layer as reported here, have not been studied.

While the optical response of ultrathin, semi-transparent Au island films can be conveniently measured using transmission spectroscopy, a detailed study of the morphology requires high-resolution imaging techniques. Transmission electron microscopy (TEM), commonly used for characterization of film structure down to atomic resolution, provides a quantitative description of the 2D projection of the island ensemble,\textsuperscript{34-37} but involves highly complex sample preparation due to the difficulty in separating the island film from the substrate while leaving the film intact. A better choice is scanning electron microscopy (SEM) imaging, which requires no particular sample preparation and allows imaging of Au island films with a resolution of several nm, as demonstrated with silicon\textsuperscript{8} and titania\textsuperscript{38} substrates. In the present work application of high-resolution SEM (HR-SEM) enables imaging of Au island films on insulating glass substrate at a high resolution. The two-dimensional images obtained by HR-SEM are complemented here by the three-dimensional atomic force microscopy (AFM) imaging, the latter providing sub-nm sensitivity in the perpendicular direction. Combination of the two imaging techniques provides information on the shape of the Au islands as well as insight into the mechanism of film growth.

The relationship between morphology and optical properties of such films has direct bearing on the sensitivity and optimization of T-SPR measurements, and is the subject of the present work.

**Experimental Section**

**Chemicals:** Chloroform (Biolab, AR) was passed through a column of activated basic alumina. Ethanol (Merck, AR), isopropanol (Frutarom, Israel), H\textsubscript{2}O\textsubscript{2} (30\%, Frutarom, Israel), H\textsubscript{2}SO\textsubscript{4} (95-98\%, Palacid, Israel), and 3-mercaptopropyl trimethoxysilane (MPTS) (97\%, Aldrich) were used as received. Water was triply distilled. The gas used was purified house nitrogen (from liquid N\textsubscript{2}).

**Gold film preparation:** Glass slides (10x18 mm\textsuperscript{2}) No. 2 (Menzel-Glazer, Germany), were immersed in freshly prepared ‘piranha’ solution (1:3 H\textsubscript{2}O\textsubscript{2} 30\% : H\textsubscript{2}SO\textsubscript{4} 95-98\%) for 15 min and rinsed with triply distilled water. (\textit{Caution: Piranha solution reacts violently with organic materials and should be handled with extreme care.}) This procedure was repeated twice, after which the slides were rinsed with ethanol, dried under a nitrogen stream, and held for ca. 10 min at 100\(^{\circ}\)C. The slides were immersed for 10 min in a mixture of 1.9 ml MPTS, 1.4 ml water and 100 ml 2-propanol which was brought to reflux, then rinsed with 2-propanol, dried under a nitrogen stream, and cured in an oven at 100-107\(^{\circ}\)C for 8 min. The silanization procedure was carried out 3 times.\textsuperscript{31} The silanized glass slides were mounted in a cryo-HV evaporator (Key High Vacuum) equipped with a Maxtek TM-100 thickness monitor for evaporation of the ultrathin Au films. Homogeneous Au deposition was achieved by moderate rotation of
the substrate plate. Gold (99.99%, Holland-Moran, Israel) was evaporated from a tungsten boat at 2-4 x 10⁻⁶ Torr, at a deposition rate of 0.005-0.01 nm s⁻¹. Post-deposition annealing of Au-covered slides was carried out in air at 200°C for 20 h, using a Ney Vulcan 3-550 oven. The heating rate was 5°C min⁻¹, and the annealed slides were left to cool in air to room temperature.

**UV/Vis spectroscopy:** Measurements were carried out ex situ (in air) using a Varian CARY 50 UV/VIS/NIR spectrophotometer with a specially designed holder.² The scan rate was 600 nm min⁻¹, and the bandwidth of the light source in the UV/Vis region was 1.0 nm. A baseline correction procedure (the spectrum of air was taken as baseline) was executed prior to each measurement session.

**Atomic force microscopy (AFM):** AFM images were recorded in air using Molecular Imaging PicoScan™ (Pico IC) instrument operated in the acoustic AC (AAC) mode. The cantilevers used were NSC12 series of ultrasharp silicon (MikroMash, Estonia), with a resonant frequency of 100-200 kHz and an average tip radius of ≈10 nm.

**High-resolution scanning electron microscopy (HR-SEM):** Images were obtained using a JSM-6700F high-resolution scanning electron microscope with a cold field emission electron source and upper built-in SE detector. Low energy SE signal suppression was performed to reduce the charging effect in the SE images, particularly important for the 1.0 and 2.5 nm samples. Statistical analysis of HR-SEM images was carried out using ImageJ image processing software.

**Results and Discussion**

**Preparation and stabilization of Au island films**

Ultrathin Au island films with nominal thicknesses of 1.0, 2.5, 5.0, 7.5, 10.0, and 15.0 nm were evaporated on MPTS-modified glass substrates at an evaporation rate of 0.005-0.01 nm sec⁻¹. The excellent adhesion provided by MPTS interlayers to Au films evaporated on glass is well established.²,³¹ Annealing has been used for tuning the optical properties (intensity and wavelength of the localized SP band) and morphology of Au island films.¹,²,²³,³⁹ Here annealing was carried out by heating in air to 200°C for 20 h. The relatively low temperature and long annealing time (we previously used 250°C for 3-4 h for annealing of films on bare substrates²,²³) were chosen to protect the organic adhesive layer (low temperature) while enabling Au island reorganization (long time). Hence, 2.5 nm Au island films, both unannealed and annealed, passed successfully the adhesive tape test³¹ (Scotch, Magic transparent), demonstrating the good adhesion provided by the MPTS interlayer and its stability under the annealing conditions. Transmission UV/Vis spectrum was recorded for each substrate after Au deposition, and samples that showed substantial deviation from the average spectrum were discarded (about 15% of the samples).
All the samples were stabilized by dipping in 1:1 CHCl₃/EtOH (solvents commonly used for self-assembly of organic mono/multilayers⁴⁰,⁴¹) and drying under a stream of nitrogen. The indication for stability of the Au island films was the SP extinction peak measured in air, which stopped changing after about 10 min in the solution (this time varied somewhat between samples). Figure 1 demonstrates the effect of solvent on the optical properties of 2.5 nm films. The immersion induces a small blue shift of the optical spectrum and a marked decrease in the optical density; the same trend is observed for the other thicknesses, as well as with other solvents, e.g., water (not shown). These spectral changes are attributed to the effect of wetting and drying on the fine morphology of the Au islands, an effect known for Ag island films,²⁴,⁴²,⁴⁴ directly influencing the Au surface plasmon absorbance.

**Morphology of Au island films**

Figure 2 shows HR-SEM and AFM images of the Au films (1.0-15.0 nm nominal thickness). In general, the average island size increases with thickness; a situation close to percolation is seen at about 15.0 nm for the unannealed film, in agreement with the optical results discussed later. The percolation threshold is sensitive to the film thickness, the evaporation rate and the annealing process. **The effect of the evaporation rate is particularly intriguing; hence, evaporation of 15.0 nm Au on similar substrates at faster rates (0.05-0.1 nm sec⁻¹) produces continuous films on both annealed and unannealed samples,³³ while at the lower rates used here an island morphology is obtained.** Under the present conditions annealing leads to an increase in the average area of individual islands and of the average distance between islands, as well as to a change in the island shape. These changes are quite similar to those observed with other substrates,²²,²³ suggesting that island mobility and coalescence is the predominant mechanism responsible for the morphology change induced by annealing.

HR-SEM and AFM studies of 2.5 nm Au films before and after solvent stabilization (see above) did not reveal any visible change in the island organization or morphology. This suggests that the mechanism responsible for the marked change in the optical spectra upon immersion and drying (Figure 1) involves structural changes that are not visible in the 2D projection of the HR-SEM or in the AFM topography of the islands, e.g., possible alteration of the shape at the island/substrate interface. This intriguing effect requires further study.

Statistical analysis of the HR-SEM images was carried out using ImageJ image processing software. The procedure included threshold image intensity adjustment that enabled the software to identify the islands, thus providing a good estimate of the Au coverage. In the 1.0 nm unannealed sample the islands were inseparable by the software, and this sample was therefore not included in the analysis. The overall area fraction of the Au islands was produced by analysis of the Au coverage (Figure 3). In general, the area fraction of unannealed Au island films is larger and grows faster with thickness than that of the corresponding annealed films. This reflects the effect of annealing, i.e.,
joining adjacent islands while increasing the average island height as well as the average separation between islands.

The average island area was also extracted using the image processing software. The average separation between islands, not obtainable by the image processing procedure, was derived manually by superposing a grid on each image and measuring the separation between islands along all the lines in the grid, and averaging. This procedure is rather inaccurate for the 1.0 and 2.5 nm films due to the small inter-island separation, as seen in the images. For the 2.5 nm samples an array of circular-shaped islands was assumed and the average separation between islands was estimated from the overall area fraction and the average island size. For the 1.0 nm annealed films these assumptions cannot be used due to the formation of 'chains' of islands, hence the 1.0 nm films were not included in the analysis.

The results are shown in Figures 4 and 5. For the unannealed films the average island area (Figure 4) grows substantially as the gold thickness increases, while the average separation between the islands (Figure 5) increases moderately. Intuitively the separation between islands in the unannealed films should not increase, or even decrease, as more material is added. The results therefore suggest that Au island coalescence and reshaping proceeds during Au evaporation on the time scale of seconds, influencing the morphology of unannealed films. This process is enhanced by a secondary annealing effect during evaporation (induced by the heated boat), more pronounced for longer evaporation (higher thicknesses). In the annealed films the average island area (Figure 4) and the average separation between the islands (Figure 5) grow substantially as the Au thickness increase, implying a marked increase in island height of the annealed films.

Information on the Au island height (z-scale information) can be obtained by AFM imaging. Figure 2 shows AAC mode AFM images of Au films similar to those analyzed by HR-SEM. The Au islands appear larger in diameter, more rounded and closer to each other in the AFM images compared to the corresponding HR-SEM images, resulting from AFM tip convolution. Hence the lateral island dimensions in the AFM images are not reliable, yet AFM provides viable information on the island height, not available in the 2D HR-SEM imaging. The data provided by the two techniques are complementary, and when combined, can give valuable estimates of the island shape.

In order to address the AFM tip convolution issue in the present case, the total number of Au islands, counted directly from the HR-SEM and AFM images of unannealed films (Figure 2), were compared for different nominal thicknesses (Table 1). As expected, the Au island density in the HR-SEM images is higher than that in the corresponding AFM images. The difference in island density (Table 1) decreases from 12% (2.5 nm films) to 7% (5.0 nm films) and is close to zero for 7.5 nm film and above. Combining these data with the measured average separation between islands (Figure 5) indicates an approximate lateral limit of ca. 10 nm for true island separation in our AFM imaging, in agreement with the tip radius (≤10 nm according to specifications).
The AFM results are presented in Figure 6 as the average island height (obtained by statistical analysis of the AFM images in Figure 2) vs. Au nominal thickness. Also plotted in Figure 6 are (i) the theoretical thickness of a homogeneous, continuous film grown to the nominal thickness, i.e., a straight line with a 45° slope; (ii), (iii) average island height calculated from the area fraction data (Figure 3) (nominal thickness/area fraction) for the unannealed and annealed films, respectively. As seen in Figure 6, the AFM measured average height of the unannealed films is lower than the thickness calculated from the area fraction, and lower even from the nominal thickness. This again is a manifestation of substantial tip convolution, as the largest average separation between islands for unannealed films is ca. 15 nm (for the 15 nm film, see Figure 5). For annealed films the average AFM measured height is lower than that calculated from the area fraction for films below 5.0 nm (nominal thickness) (Figure 6), which is the thickness where the separation between islands is also ca. 15.0 nm (Figure 5). Above 5.0 nm (nominal thickness) the AFM measured island height of annealed films follows fairly closely the height calculated from the area fraction, giving somewhat larger values (probably associated with the island shape) and indicating little, if any, tip convolution for these samples.

Evolution of the Au island film morphology with increasing thickness, as observed in this study, raises the issue of high total island area at percolation (about 80% surface coverage for unannealed films near percolation, see Figure 3). This indicates the major impact of island mobility, coalescence and reshaping during evaporation on the film morphology. The rather small difference of 12% in island density observed in AFM vs. HR-SEM images of 2.5 nm films (even smaller for larger thicknesses) (Table 1) suggests that the 2-D shape of the islands seen in the AFM images is generally correct, as also revealed by comparison with HR-SEM images (Figure 2). A magnified image of a 2.5 nm unannealed film shows round-shaped islands (Figure 7 a), which can be described as oblate ellipsoids. The shape of contacting islands is close to that of individual ones, indicating a small degree of island coalescence. AFM images of the 5.0 and 7.5 nm films show considerably more interconnected chains (Figure 7 b, c) with partial coalescence of smaller islands, promoting lower total island area and an increase in the average island height. The percolation threshold is thus reached at a higher average coverage than the one expected for simple growth without island mobility and coalescence (50% and 59% for triangular and square lattices, respectively).

It should be noted that a more quantitative evaluation of the coalescence process is complicated by the induced temperature rise during the evaporation, influencing island mobility and aggregation.

Optical properties of Au island films

Unannealed and annealed Au island films on silanized glass substrates were characterized by transmission UV/Vis spectroscopy after stabilization in a solvent (see Preparation and Stabilization). As shown previously for Au island films on bare glass,
a red shift and an increase in the optical density are observed upon increasing the nominal thickness (Figure 8). The effect of annealing is seen in Figures 1 and 8; annealing induces a blue shift in the spectrum (up to 164 nm) and a decrease in the optical density (up to 0.15 a.u.). The SP band is completely lost in the spectrum of the 15.0 nm unannealed Au film (Figure 8 a), indicating a transition from island morphology to a continuous film. This is in agreement with the HR-SEM imaging (Figures 8 c), where a near-percolation situation, with micron-size connected Au areas, is observed for the 15.0 nm unannealed film. Careful inspection of the spectrum of the 1.0 nm annealed Au film reveals a longitudinal plasmon at longer wavelengths (700-800 nm) characteristic of chains of islands, as evident in the HR-SEM image of the corresponding film (Figure 2).

**Conclusions**

Evaporation of 1.0-15.0 nm (nominal thickness) gold at a slow rate (0.005-0.01 nm s$^{-1}$) on MPTS-treated glass substrates provides arrays of island-shaped Au films, stabilized by the MPTS adhesion layer. As previously shown by us for Au island films on untreated transparent substrates, the films display an intense surface plasmon (SP) absorbance in the Vis-NIR range, which is sensitive to the Au thickness, the evaporation conditions, post-deposition annealing, and exposure to solvents. Hence, immersion in 1:1 CHCl$_3$/EtOH solution led to a marked change in the SP absorbance, while no corresponding change in morphology could be seen by HR-SEM imaging, a point to be further investigated. As shown previously, increasing the Au nominal thickness promotes an increase in the intensity and a red shift of the Au SP band, whereas annealing leads to a decrease in the intensity and a blue shift of the SP band.

Analysis of HR-SEM and AFM images of the Au island films shows that the average island dimensions (lateral diameter and height) increase with nominal thickness. Annealing increases the average area of individual islands, the average island height, and the average separation between islands. Therefore, the fractional coverage of the glass by the Au is larger and increases faster for unannealed films. HR-SEM imaging and spectroscopic data both indicate a percolation transition around 15.0 nm (nominal thickness) for the unannealed (but not the annealed) films, exhibited as micron-scale conducting paths (HR-SEM imaging) and disappearance of the Au SP band (transmission spectroscopy). The combination of HR-SEM and AFM imaging proved to be rather powerful in providing a realistic view of the island shape.

Of the Au island films studied here, annealed films of 2.5-10.0 nm nominal thickness are relatively stable and display a well-defined SP band, thus being particularly promising for T-SPR spectroscopy and sensing applications.

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References

(3) Lahav, M.; Vaskevich, A.; Rubinstein, I. Submitted for publication.
FIGURE CAPTIONS

**Figure 1.** UV/Vis spectra of 2.5 nm gold films on silanized glass (measured *ex situ*), immediately after evaporation (dashed line) and after dipping in 1:1 CHCl₃/EtOH solution until stabilization of the SP absorption band was observed (solid line).

**Figure 2.** AAC mode AFM and HR-SEM images (400 x 400 nm²) of ultrathin gold island films on silanized glass. Nominal thickness (left), z-scale (under each AFM image) and preparation conditions (top) are indicated.

**Figure 3.** Fractional coverage of the glass by Au islands vs. Au nominal thickness. Data obtained by image processing (ImageJ software) of HR-SEM images.

**Figure 4.** Average area of individual Au islands vs. Au nominal thickness. Data obtained by image processing (ImageJ software) of HR-SEM images.

**Figure 5.** Average separation between islands vs. Au nominal thickness. Data obtained by statistical analysis of HR-SEM images.

**Figure 6.** Average height of Au islands vs. Au nominal thickness, showing data obtained by statistical analysis of AFM images (squares); data calculated from the Au area fraction (circles); and nominal thickness (dashed line). Open and full symbols represent unannealed and annealed samples, respectively. Lines through the experimental points are drawn as guides to the eye.

**Figure 7.** 3D AFM images (150 x150 nm²) of 2.5 nm (a), 5.0 nm (b) and 7.5 nm (c) Au island films. Arrows indicates coalescence of islands. Z-scale bar: 5 nm (a), 10 nm (b, c).

**Figure 8.** Transmission UV/Vis spectra of ultrathin gold island films on silanized glass, (a) unannealed and (b) annealed 20 h at 200°C. Nominal thicknesses are indicated. (c) is a HR-SEM image of a 15.0 nm unannealed Au film.
Table 1. Island density in unannealed Au island films on silanized glass.

<table>
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<th>Au island density, μm²</th>
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<td>HR-SEM image</td>
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Figure 1
Figure 2
Figure 5

Figure 6
Figure 8
TOC Graphic and Summary.

The morphology of ultrathin gold island films evaporated on silanized glass was studied by AFM and HR-SEM, and their optical properties examined using transmission UV/Vis spectroscopy. The localized surface plasmon absorbance shows a strong dependence on the film morphology, the latter determined by the Au thickness, deposition conditions and annealing.
3.4. Distance Sensitivity of Transmission Surface Plasmon 
Resonance (T-SPR) Spectroscopy. Self-Assembled Multilayers 
on Evaporated Gold Island Films


Submitted.
Distance Sensitivity of Transmission Surface Plasmon Resonance (T-SPR) Spectroscopy. Self-Assembled Multilayers on Evaporated Gold Island Films

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The distance dependence of the localized surface plasmon (SP) extinction of discontinuous gold films is a crucial issue in the application of transmission surface plasmon resonance (T-SPR) spectroscopy to chemical and biological sensing. This derives from the usual sensing configuration, where an analyte binds to a selective receptor layer on the gold film at a certain distance from the metal surface. In the present work the distance sensitivity of T-SPR spectroscopy of 1.0-5.0 nm (nominal thickness) gold island films evaporated on silanized glass substrates is studied using coordination-based self-assembled multilayers, offering thickness tuning in the range from ~1 to ~15 nm. The morphology, composition and optical properties of the Au/multilayer systems were studied at each step of multilayer construction. High-resolution scanning electron microscopy (HR-SEM) showed no apparent change in the underlying Au islands, while atomic force microscopy (AFM) indicated flattening of the surface topography during multilayer construction. A regular growth mode of the organic layers was substantiated...
by X-ray photoelectron spectroscopy (XPS). Transmission UV-vis spectra showed an increase of the extinction and a red shift of the maximum of the SP band upon addition of organic layers, establishing the distance dependence of the Au SP absorbance. The distance sensitivity of T-SPR spectroscopy can be varied using characteristic substrate parameters, i.e., Au nominal thickness and annealing. In particular, effective sensitivity up to a distance of at least 15 nm is demonstrated with 5 nm annealed Au films. It is shown that intensity measurements, particularly in the plasmon intensity change (PIC) presentation, are superior to the usually measured plasmon band position, offering better accuracy and the possibility of measuring at a single wavelength with maximum sensitivity. The present distance sensitivity results provide the basis for further development of T-SPR transducers based on receptor-coated Au island films.

Keywords: Gold, surface plasmon, island films, self-assembly, multilayer, sensor.

Introduction

Transmission UV-vis spectra of Au and Ag island films, as well as those of structures comprised of metal nanoparticles, exhibit a characteristic absorption band attributed to excitation of localized surface plasmon (SP) polaritons. The conditions for SP resonance depend on the metal film morphology, i.e., island size, shape, spatial organization, and the dielectric properties of the contacting medium. The dependence of the SP absorption band (wavelength, intensity) of metal island films on the dielectric constant of bathing solvents is well established. Recently we and others have demonstrated sensitivity of the SP band of Au island films to various adsorbed molecular layers. The method, termed transmission surface plasmon resonance (T-SPR) spectroscopy, offers a combination of high sensitivity and simple experimental requirements. T-SPR spectroscopy was shown to be applicable to both chemically and physically adsorbed molecules, in liquid or gas phase. The T-SPR approach is particularly promising for biosensing, and the first examples have been published recently.

Application of T-SPR spectroscopy to actual sensing, and particularly to biosensing, involves construction of complex interfaces, promoting selective binding of desired analytes while preventing non-specific binding. Systems of this kind would normally require a multilayer structure including selective receptors as well as blocking layers, all assembled on the metal island film. The target analyte molecules would therefore be bound to a receptor layer at a certain distance from the metal island surface. Consequently, the sensitivity and distance-dependence of T-SPR response to
analyte binding becomes a major issue in the design and optimization of sensing elements.

Studies of distance-dependent properties of evanescent waves in metal island films have been stimulated by the development of the electromagnetic theory of surface enhanced Raman spectroscopy (SERS).\textsuperscript{19} Several experimental approaches have been used to achieve controlled separation between the metal surface and probe molecules in SERS studies, i.e., deposition of ultrathin polymeric films\textsuperscript{20,21} or silica overcoats;\textsuperscript{22-25} Langmuir-Blodgett multilayers;\textsuperscript{26,27} and self-assembled monolayers (SAMs).\textsuperscript{28,29} These methods provide a separation in the range of $\sim$2-15 nm. Van Duyne, Schatz and coworkers\textsuperscript{10,30} studied the distance dependence of the SP absorbance of Ag and Au nanoparticle films of characteristic dimensions that are an order-of-magnitude larger than the average island dimensions (diameter, height) of the Au island films studied here.\textsuperscript{31}

In the present study the distance sensitivity of the T-SPR response of evaporated Au island films is evaluated using coordination-based self-assembled multilayers, previously studied by us on continuous, evaporated Au substrates.\textsuperscript{32-35} This approach is extended here to the layer-by-layer construction of similar multilayers on Au island films. The multilayers are prepared by coordination self-assembly, including binding of Zr$^{4+}$ ions to a self-assembled monolayer of disulfide-dihydroxamate anchor molecules on the Au followed by alternate binding of layers of bifunctional tetrahydroxamate molecules and Zr$^{4+}$ ions (Fig. 1). The regular growth of the multilayer provides a tunable distance in the range from $\sim$1 to $\sim$15 nm, enabling to study the distance dependence of the optical response of Au island films and affording an excellent simulation of actual T-SPR sensing.\textsuperscript{36,37}

The substrates used here were 1.0–5.0 nm (nominal thickness) Au island films evaporated on mercaptopropyl trimethoxysilane (MPTS) modified glass, combining excellent adhesion of the metal to the substrate and tunable absorbance.\textsuperscript{31} The morphology and optical properties of the multilayer-coated Au island films were studied by high-resolution scanning electron microscopy (HR-SEM), atom force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and transmission UV-vis spectroscopy. Superior distance sensitivity is observed with 5.0 nm annealed Au films on silanized glass, where essentially no deviation from linear response was seen in the measured thickness range (up to 11 organic layers, ca. 15 nm).
Experimental Section

Chemicals: Molecules 1 and 2 (Fig. 1) were synthesized as previously reported. Zirconium acetylacetonate (ZrAcAc, Fluka, purum) was used without further purification. Chloroform (Biolab, AR) was passed through a column of activated basic alumina. Ethanol (Merck, AR), isopropanol (Frutarom, Analytical), H₂O₂ (30%, Frutarom), H₂SO₄ (95-98%, Palacid), 3-mercaptopropyl trimethoxysilane (MPTS) (Aldrich, 97%) were used as received. Water was triply distilled. The gas used was purified house nitrogen (from liquid N₂).

Gold film preparation: Glass slides (10x18 mm²), No. 2 (Menzel-Glaser, Germany), were immersed in freshly prepared ‘piranha’ solution (hot 1:3 H₂O₂ 30% : H₂SO₄ 95-98%) for 15 min and rinsed with triply distilled water. (Caution: Piranha solution reacts violently with organic materials and should be handled with extreme care.) This procedure was repeated twice, after which the slides were rinsed with ethanol, dried under a nitrogen stream, and held for ca. 10 min at 100°C. The slides were immersed for 10 min in a mixture of 1.9 ml MPTS, 1.4 ml water and 100 ml isopropanol which was brought to reflux, then rinsed with isopropanol, dried under a nitrogen stream, and cured in an oven at 100-107°C for 8 min. The silanization procedure was carried out 3 times. The silanized glass slides were mounted in a cryo-HV evaporator (Key High Vacuum) equipped with a Maxtek TM-100 thickness monitor for evaporation of the ultrathin Au films. Homogeneous Au deposition was achieved by moderate rotation of the substrate plate. Gold (99.99%, Holland-Moran, Israel) was evaporated from a tungsten boat at 2-4 x 10⁻⁶ Torr, at a deposition rate of 0.005-0.01 nm s⁻¹. Post-deposition annealing of Au-covered slides was carried out in air at 200°C for 20 h, using a Ney Vulcan 3-550 oven. The heating rate was 5°C min⁻¹, and the annealed slides were left to cool in air to room temperature.

Multilayer self-assembly: Prior to self-assembly the Au island substrates were stabilized in CHCl₃/EtOH (1:1), as previously described. Monolayers of the anchor molecule 1 (Fig. 1) were adsorbed from a 3 mM CHCl₃/EtOH (1:1) solution of the molecule overnight, followed by rinsing with chloroform and ethanol and immersion in ethanol for 20 min. Zr(IV) was bound to the monolayer of 1 from a ZrAcAc solution (1 mM in ethanol) for 1 h, followed by rinsing and immersion in ethanol for 10 min. The repeat unit 2 (Fig. 1) was coordinatively bound by exposure of the surface complex to a 3 mM solution of the tetrahydroxamate 2 in ethanol overnight, followed by ethanol rinse. The sample was then treated repeatedly with the metal ion and the
organic tetrahydroxamate, resulting in a multilayer structure with a controlled number of layers.

UV-vis spectroscopy: Measurements were carried out ex situ (in air) using a Varian CARY 50 UV/VIS/NIR spectrophotometer with a specially designed holder. The scan rate was 600 nm min⁻¹, and the bandwidth of the light source in the UV-vis region was 1.0 nm. A baseline correction procedure (the spectrum of air was taken as baseline) was executed prior to each measurement session. A transmission UV-vis spectrum was recorded for each substrate after Au deposition, and samples that showed substantial deviation from the average spectrum were discarded (about 15% of the samples). All the samples were stabilized by dipping in 1:1 CHCl₃/EtOH (the solvents used for self-assembly of the organic layers) and drying under a stream of nitrogen. The indication for stability of the Au island films was the SP extinction peak measured in air, which stopped changing after about 10 min in the solution (this time varied somewhat between samples).

Atomic force microscopy (AFM): AFM images were recorded in air using Molecular Imaging PicoScan™ (Pico IC) instrument operated in the acoustic AC (AAC) mode. The cantilevers used were NSC12 series of ultrasharp silicon (MikroMasch, Estonia), with a resonant frequency of 100-200 kHz and an average tip radius of ≤10 nm.

X-ray photoelectron spectroscopy (XPS): XPS measurements were carried out with a Kratos Axis-HS XPS system, using monochromatized Al (Ka) X-ray source (1486.6 eV). Elimination of beam induced damage effects was achieved by first studying the evolution of these effects and then performing the analysis on fresh spots using optimal experimental conditions.

High-resolution scanning electron microscopy (HR-SEM): Images were obtained using a JSM-6700F high-resolution scanning electron microscope with a cold field emission electron source and an upper built-in SE detector. Low energy SE signal suppression was performed to reduce the charging effect in the SE images, particularly important with the 1.0 and 2.5 nm samples.
Multilayer self-assembly on gold island films

Ultrathin gold films evaporated on MPTS-modified glass substrates show excellent adhesion to the substrate, favoring their use as T-SPR based sensors. Adjustment of the morphology and optical properties of such films can be achieved by variation of the film nominal thickness, evaporation rate and post-deposition annealing conditions. In the present case Au island films of 1.0, 2.5 and 5.0 nm nominal thickness, unannealed and annealed (200°C for 20 h), served as substrates for the layer-by-layer assembly of metal-organic multilayers. Details on the Au island film properties are given elsewhere.31

Construction of coordination-based self-assembled multilayers on the Au island films generally followed our previously published methodology,32-34 shown schematically in Fig. 1. The anchor monolayer adsorbed directly on the Au islands comprised the disulfide bishydroxamate molecule 1, while the repeat unit was the bifunctional tetrahydroxamate ligand 2, coordinated via Zr⁴⁺ ions. We have recently modified the multilayer preparation scheme, replacing ZrCl₂ with ZrAcAc in the ion-binding step.35 Multilayer construction occurs by alternate binding of Zr(IV) and ligand 2, resulting in the addition of a single organic layer in each step. Detailed characterization of such multilayers prepared on continuous, 100 nm thick gold substrate using ellipsometry, contact angle measurements and XPS, showed linear growth of a multilayer with nearly ideal 1:1 metal:ligand stoichiometry, while AFM height measurements of scratched multilayers gave a thickness increase of 1.4±0.17 nm per step.35

Morphology of coordination-based multilayers constructed on Au island films

Multilayers were constructed on Au films of 1.0, 2.5 and 5.0 nm (nominal thickness), unannealed and annealed. T-SPR measurements showed that the 1.0 nm Au films are not sensitive enough for monitoring multilayer construction (see below), hence the morphology study was limited to the 2.5 and 5.0 nm films. Coordination multilayers on Au island films were characterized using a combination of HR-SEM and AFM. HR-SEM imaging by SE (secondary electrons) provides a surface morphology contrast which is enhanced by BSE (backscattered electrons) induced SE at the Au island location below the multilayers. The images thus appear transparent to the organic layer, enabling comparison of the Au island morphology before and after multilayer formation, while AFM provides complementary information on changes in
the surface topography. The number of layers in each sample was chosen according to the sensitivity of the SP absorption to thickness increase.

HR-SEM images of bare and multilayer-covered Au island films (Fig. 2) are visually similar, showing the same surface density and shape of the Au islands. This indicates that the good adhesion of Au islands to the silanized glass prevents noticeable island shifting and reshaping during multilayer construction. For example, the number of islands (counted manually) in a 200x200 nm² area in the 2.5 nm annealed Au films before and after multilayer construction is 114 and 116, respectively (practically the same). The decreased sharpness in the HR-SEM images of multilayer-covered samples is attributed to reduced SE resolution in the images of these samples. It mainly corresponds to the SE MFP (mean free path), which is ca. 5.5 nm for carbon (at the multilayer surface) and 1 nm at bare Au island regions. The SE induced by BSE spread through the multilayer, which further contributes to delocalization of the SE signal at the multilayer surface.

AFM images of bare and multilayer-covered Au island films are also shown in Fig. 2. The AAC AFM mode used here is sensitive to soft matter on the corrugated surface, i.e., the tip does not penetrate the organic layer and follows the surface topography. The average AFM-derived lateral dimension of the islands in the 2.5 nm films appears larger after multilayer construction; while there is a decrease in the number of islands in the AFM images of 2.5 nm films (more pronounced with the unannealed sample) upon multilayer construction, in the 5.0 nm films the island density remains almost identical. The AFM images are influenced by the tip diameter (ca. 10 nm) which is similar to, or larger than, the average separation between islands (δ-6 nm for 2.5 nm and unannealed 5.0 nm films; δ=12 nm for annealed 5.0 nm films). In the case of the ‘rolling hills’ topography typical of island films, the upper part of the grains would be imaged correctly, while the inter-particle region is affected by tip convolution. In the case of the 5.0 nm films, where the 2D AFM-imaged morphology is nearly unaffected by the multilayer (Fig. 2), the change in topography is evident in the 3D images (Fig. 3), where substantial flattening is seen with sharp features disappearing in the images of the multilayer-covered island films.

The step-by-step process of multilayer construction was also evaluated by XPS. Fig. 4 shows normalized atomic concentrations of C, N and Zr vs. the number of organic layers assembled on unannealed and annealed 2.5 nm Au island films. The linear increase in log [intensity ratio] of the overlayer elements (Zr, C, N vs. Au) with the number of organic layers indicates regular growth of the film thickness, as shown for coordination multilayers grown on continuous, 100 nm thick gold substrate.
is therefore concluded that the construction of coordination multilayers on the Au island films proceeds in a regular fashion, such that the contribution of each additional organic layer to the overall film thickness is approximately the same. The thickness increment per added monolayer is assumed to be ca. 1.4 nm, as measured on continuous gold substrates (see above).35

Transmission spectra of gold island films

Series of transmission UV-vis spectra were measured during construction of multilayer film on 1.0, 2.5, and 5.0 nm Au films, unannealed and annealed. After each added layer the sample was rinsed and dried and a transmission spectrum was taken in air. The spectra of 1.0 nm Au films were not sensitive enough for effectively monitoring of multilayer construction, therefore the analysis below concentrates on 2.5 and 5.0 nm films. Representative spectra of 2.5 and 5.0 nm Au films are shown in Fig. 5a-d. In all cases a similar development is seen in the spectra, i.e., an increase of the extinction and a red shift of the maximum of the SP band upon addition of organic layers. The system behavior qualitatively conforms with the expected response of the SP band to an increase of the effective dielectric constant near the surface of Au islands.1,43

While evolution of the transmission spectra of the different films is qualitatively similar in the first few steps of multilayer self-assembly, noted differences are observed at increased thicknesses (Fig. 5a-d). The best distance sensitivity is obtained with the 5.0 nm annealed film, where the SP band intensity increases nearly linearly throughout the entire measured range (11 organic layers, including the anchor layer, ca. 15 nm overall thickness) (Fig. 5d). For all other substrates the change in the SP intensity decreases with increasing number of layers (Fig. 5a-c), indicating loss of distance sensitivity and saturation of the signal. Fig. 5e shows the plasmon intensity change (PIC)8,9 for the 5.0 nm annealed Au substrate, emphasizing the superior distance sensitivity of the system. Fig. 6 summarizes the changes in two characteristic parameters of the T-SPR spectra, i.e., wavelength (Fig. 6a) and intensity (Fig. 6b) of the SP maximum absorbance, with the number of organic layers assembled on 1.0, 2.5, and 5.0 nm Au island films, unannealed and annealed. Both parameters vary monotonously with increasing number of layers, approaching saturation at a certain thickness. A noted exception is the 5.0 nm annealed substrate, where the intensity change does not show significant deviation from linearity in the studied thickness range, i.e., 11 organic layers.
The 2.5 and 5.0 nm annealed Au island films, and in particular the latter, show excellent distance sensitivity of the SP intensity up to, and beyond, a distance equivalent of 11 organic layers (ca. 15 nm) (Fig. 6c). Comparison with morphology data (Fig. 2) suggests that the sensitivity is related to the island height and/or average separation between islands, increased by annealing.\textsuperscript{31}

**Conclusions**

The sensitivity and distance dependence of Au island films in T-SPR measurements were evaluated using layer-by-layer construction of coordination-based self-assembled multilayers. The multilayer system has been shown previously to afford regular growth on thick, continuous Au films, with a thickness increment of ca. 1.4 nm per step. The present study showed that a similar linear growth mode applies to the multilayer constructed on discontinuous Au island films. The morphology of bare and multilayer-covered Au island films evaporated on silanized glass was studied by combined HR-SEM (showing the metal islands) and AFM (showing the 3D topography) images. The Au islands appear to be unaffected by the multilayer growth, while the topography shows significant flattening induced by the organic overlayer.

The layer-by-layer growth of the metal-organic overlayer on Au island films (1.0, 2.5 and 5.0 nm nominal thickness, unannealed or annealed 20 h at 200\textdegree C) was monitored at each step by T-SPR spectroscopy. The distance dependence of the SP absorbance is strongly dependent on the film preparation conditions, i.e., nominal thickness and annealing. The present results do not, however, provide evidence as to the influence of each structural parameter, as all the characteristic dimensions (island diameter, height, shape, separation) vary between samples.\textsuperscript{31}

The best distance sensitivity of the SP extinction was obtained with 5.0 nm annealed Au island films. For these films the sensitivity of the SP intensity to the addition of organic layers was nearly constant up to a distance from the Au substrate corresponding to 11 organic layers (ca. 15 nm). This value is a lower limit for the distance sensitivity of the system, as little deviation from linearity is observed at the highest thickness studied here.

The present results on the distance sensitivity of T-SPR spectroscopy using evaporated Au island films are promising in terms of application of the technique to the design of transducers for chemical or biological sensing, usually involving receptor layers on the transducer surface. A distance sensitivity of 15 nm (lower limit) from the Au island surface provides ample room for binding of bulky biological receptors to
the island film while maintaining reasonable sensitivity in the sensing event, i.e., binding of a specific analyte to the receptor layer. We have recently demonstrated the applicability of T-SPR sensing to specific avidin recognition using a biotinylated Au island surface.\textsuperscript{13}

While in other systems the quantity commonly measured is the wavelength of the SP band maximum, we emphasize band intensity measurements as superior in several respects. First, determination of the wavelength of the band maximum may be quite inaccurate, particularly with broad SP bands, whereas determination of the maximal intensity is simple and accurate in all cases. Second, evaluation of changes in the band position requires, by definition, spectral measurements, while monitoring changes in the band intensity can be done at a single wavelength, thus simplifying substantially the instrumentation. Particularly attractive for sensing applications is measurement of the plasmon intensity change (PIC), i.e., the maximum of the difference spectrum after subtracting the spectrum of the substrate (Figs. 5e, 6c). As seen in Fig. 5e, the position of the PIC is nearly distance independent, as previously shown by us for monolayer coverage.\textsuperscript{8} Hence, PIC measurements can be carried out at a single wavelength with maximum sensitivity, presenting a viable alternative to traditional (Kretchmann-type) SPR spectroscopy, widely used in biological sensing.

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(42) The zero-layer value of the carbon corresponds to the adhesion layer and to some contamination present on the gold grains.

Figure captions

Figure 1. Building blocks and construction scheme of the coordination-based metal-organic multilayers.

Figure 2. AAC mode AFM and HR-SEM images (500x500 nm²) of ultrathin Au island films on silanized glass before and after multilayer construction. The number of organic layers in the multilayer: 6 (2.5 nm, unannealed); 9 (5.0 nm, unannealed); 11 (2.5, 5.0 nm, annealed). A representative cross-section is shown under each AFM image.

Figure 3. 3D AFM images (200x200 nm²) of 5.0 nm unannealed and annealed Au island films before and after multilayer construction (number of organic layers as in Fig. 2). Z-scale bar in all images is 10 nm.

Figure 4. Atomic concentration ratios from XPS measurements vs. number of organic layers assembled on 2.5 nm unannealed (a) and annealed (b) Au island films. The lines are a linear fit to the data points.

Figure 5. (a) - (d) Sequential transmission UV-vis (T-SPR) spectra of 2.5 and 5.0 nm gold island films (unannealed and annealed) taken after construction of each organic layer. Dashed lines correspond to the bare gold. (e) Difference spectra (spectrum of the bare Au subtracted) for the construction of a coordination multilayer on 5.0 nm annealed Au film (data from Fig. 5d).

Figure 6. (a) Wavelength of maximum extinction, (b) maximum intensity of the SP band, and (c) plasmon intensity change (PIC), of annealed Au island films (nominal thickness indicated) during step-by-step assembly of metal-organic layers (data from Fig. 5).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
TOC figure.
4. General discussion and conclusions

The study of supramolecular structures on solid supports is of major interest both for the fundamental understanding of the structure and properties of the assembly and from the applicative point of view. A novel kind of supramolecular multilayer was constructed by our group, based on self-assembled coordination metal-ion complexes.\(^1\) The construction is carried out by addition of molecular and ion layers alternately on gold surface. This system, which enables the insertion of a 'marker' layer at a predetermined depth, and is a few nanometers thick, was ideal for the development of a new depth-profiling method using XPS. Though there are several XPS depth-profiling methods (see section 3.1.), all suffer from various limitations. We report here the development of a simple, non-destructive method which uses surface charging, a parameter which is usually considered as an experimental obstacle. In this method, we charge the surface of the dielectric overlayer with the XPS electron flood gun, creating a controllable potential gradient vertically through the sample. The local potential is probed by measuring the XPS line shifts (compared to the uncharged sample), which correlate with the vertical position of the atoms. We termed the method 'controlled surface charging'.\(^2\)

The CSC method was demonstrated with two types of multilayers, i.e. Zr(IV)-based and Ce(IV)-based multilayers. For these two systems, the potential difference across the full overlayer, \(V_o\), increases linearly with the layer thickness, suggesting that the layer is practically free of space charge. Furthermore, the absolute gradient values, associated with the vertical film resistivity, are sensitive to the layer composition; there is nearly three-fold difference in the slope of \(V_o\) versus film thickness for Zr(IV) vs. Ce(IV), which suggests a marked influence of the binding ion on the electric conductivity of the layer. However, this issue should be further investigated to understand the large difference between the samples.

Thus, a comprehensive structural analysis of several Zr(IV) and Ce(IV) based coordination multilayers was the next subject of this study (section 3.2.).\(^3\) We used \(\text{ZrCl}_4\), \(\text{Zr(AcAc)}_4\) and \([(\text{NH}_4)_2\text{Ce(NO}_3)_6]\) as the source of the binding ion in the adsorption solution. Using AFM, we followed the topography changes upon construction of the multilayer on the gold surface (section 3.2.1.). We found that binding of the anchor disulfide bishydroxamate molecule to the gold does not cause
any significant change to the morphology of the gold surface. However, binding of the metal-ion involves domain formation for all the solutions used. Yet, the roughness of the films is different and is highest for the ZrCl₄ solution. This difference exists also during the construction of the multilayer, and is accompanied by a large change in the ellipsometric parameter Δ and an excess of zirconium in XPS measurements in the case of ZrCl₄ compared to the other two salts. Measuring the thickness of 10 to 12 layers of the various multilayers by AFM shows that the ZrCl₄ multilayer is the thickest, in agreement with ellipsometry measurements. Moreover, measuring the stiffness of these multilayers showed similar stiffness for the Zr(AcAc)₄ and the Ce multilayers, and higher stiffness for the ZrCl₄ one. All those parameters suggest that the use of ZrCl₄ results in the formation of a complex multilayer with zirconia-type interlayers, distributed evenly between the organic layers.

An intriguing question is the different conductivity measured by the CSC method for multilayers prepared with ZrCl₄ and Ce(IV). Measurements of the overall potential drop (Vₒ) developed across a multilayer prepared using ZrCl₄, Ce(IV), Zr(AcAc)₄ and a mixed multilayer of ZrCl₄/Ce(IV) showed that Vₒ of the Ce(IV) and Zr(AcAc)₄ multilayer are similar, and that of the ZrCl₄ and the mixed multilayer is about 3 times higher. This means that the formation of a composite structure (when using a solution of ZrCl₄) changes not just the topography and the stiffness of the assembly but also its conductivity.

Another important issue regarding the construction of coordination-based multilayers is the preparation time (section 3.2.2.). In the existing procedure, each organic layer is adsorbed overnight, which makes the multilayer preparation impractical for the construction of a large number of layers. Thus we tried to accelerate the process by adsorption of more than one layer in each step, i.e., via the formation of coordination polymers/oligomers on the gold surface. The process was tested by adsorption from a solution which includes both the tetrahydroxamate ligand and the binding ion Ce(IV). This part of the work is preliminary, yet the results indicate formation of oligomeric units (primarily dimers) in the adsorption solution. The results suggest that the solvent and the concentration ratio between the organic ligand and the binding ion may determine the length of the oligomers, and influence the process of layers growth on the substrate.

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The construction scheme of coordination-based multilayer is basically not restricted to hydroxamates. Use of a ligand with a different functional group may provide different properties (ca. mechanical, electrical, optical). Thus we demonstrated the formation of multilayers with hydroxyquinoline (HQ) ligand (and Zr(IV)) because of the possible application of HQ complexes as light-emitters in OLEDs (see section 3.2.3.). In addition, the ability of a monolayer of disulfide bishydroxyquinoline anchor molecules to bind Al(III) (Al-HQ is the most frequently used complex in OLEDs) was shown, but the adsorption conditions still need to be optimized.

The self-assembled coordination-based multilayer system, using hydroxamates and Zr(AcAc)_4, was then utilized for the study of the distance sensitivity of T-SPR spectroscopy of Au island films (section 3.4.). Such films are of interest for a variety of sensing applications, yet, to be applicable, the films should be stable and their morphology and optical properties should be tunable. Thus we first studied the morphology and optical properties of ultrathin (1.0-15.0 nm nominal thickness), island-type gold films evaporated onto 3-mercaptopropyl trimethoxysilane (MPTS)-modified glass substrates (section 3.3.). The MPTS layer was used to improve the Au adhesion to the glass. The Au island films show an intense SP absorbance in the Vis-NIR range, which is sensitive to the Au thickness, the evaporation conditions, post-deposition annealing and exposure to solvents. In general, increasing the Au nominal thickness promotes an increase in the intensity and a red shift of the SP band, while annealing leads to a decrease in the intensity and a blue shift of the SP band.

The films were imaged by HR-SEM and AFM which show that the average island dimensions (lateral diameter and height) increase with nominal thickness. Annealing increases the average area of individual islands, the average island height, and the average separation between islands. Therefore, the fractional coverage of the glass by the Au is larger and increases faster for unannealed films. HR-SEM imaging and spectroscopic data both indicate a percolation transition around 15.0 nm (nominal thickness) for the annealed (but not the unannealed) films, exhibited as micron-scale conduction paths (HR-SEM imaging) and disappearance of the Au SP band (transmission spectroscopy). The combination of HR-SEM and AFM imaging proved to be rather powerful in providing a realistic view of the island shape.

We chose to study the sensitivity and distance dependence of Au island films of nominal thicknesses of 1.0, 2.5 and 5.0 nm (unannealed and annealed) in T-SPR
measurements by the use of layer-by-layer construction of the above coordination-based self-assembled multilayers, providing distance control on the molecular level. The growth of the layers on the island films was linear (shown by XPS) as in the case of continuous Au films. Study of the morphology of the bare and multilayer covered films by HR-SEM (showing the metal islands) and AFM (showing the 3D topography) shows that the Au islands are unaffected by the multilayer growth, but the topography shows significant flattening induced by the organic overlayer.

The construction of the layers was monitored at each step by T-SPR spectroscopy, which shows that the distance sensitivity of the SP absorbance is strongly dependent on the film preparation conditions, i.e., nominal thickness and annealing. The best distance sensitivity of the SP extinction was obtained with 5.0 nm annealed Au island films. The SP absorption intensity increased almost linearly with the adsorption of 11 organic layers (ca. 15 nm), thus determining a lower limit of the distance sensitivity of the system. Such a distance provides ample room for binding of bulky biological receptors to the island film while maintaining reasonable sensitivity in the sensing event, i.e., binding of a specific analyte to the receptor layer. Sensing applications can be based on measurement of wavelength of the SP band or the maximum extinction of the SP band. Another possibility is measuring the plasmon intensity change (PIC)\(^6\), i.e., the maximum of the difference spectrum after subtracting the spectrum of the bare substrate. The position of the PIC is nearly distance independent,\(^6\) therefore Au PIC measurements can be carried out at a single wavelength with good accuracy and high sensitivity, while simplifying the instrumentation.

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5. Future directions

The present study may be continued in the following directions:

- Construction of new coordination-based multilayers, comprising various ligands and metal-ions. For example, chiral ligands may induce rigidity and may show special optical properties; HQ-based multilayers are of interest in OLED preparation; growth of zirconia thin films in a multilayered structure may have variety of applications which are mentioned in section 3.2.

- Creation of patterns on monolayers and embed patterns within multilayers is an intriguing issue. Such patterned surfaces may be used as nanometric PCBs (Printed Circuit Boards) or as a topographic/chemical memory. Local changes in topography as well as local changes in the layer composition (e.g. insertion of ligands which differ from their surrounding neighbors in the layer) may serve as readable information. By choosing the appropriate system of ligands and binding ions, it might be possible to apply this idea to a patterned multilayer structure.

- Establishing the procedure of multilayer construction via coordination polymerization may provide a practical way for the assembly of multilayered structures.

- The CSC method of high-resolution depth-profiling using XPS may be applied to a variety of non-conductive layers, less than ca. 10 nm thick. Furthermore, the possibility of the CSC method to be used as a contactless electrical probe, capable of direct detection of local potential in thin overlayers, may be investigated.

- The study of the distance sensitivity of T-SPR spectroscopy using evaporated Au island films is promising in terms of application of the technique to the design of transducers for chemical or biological sensing, usually involving receptor layers on the transducer surface. A distance sensitivity of 15 nm (lower limit) from the Au island surface provides ample room for binding of bulky biological receptors to the island film while maintaining reasonable sensitivity in the sensing event, i.e., binding of a specific analyte to the receptor layer. We showed that the sensitivity depends on the films preparation conditions, thus one may find more sensitive films, with better distance dependence. Furthermore, the possibility of making T-SPR spectroscopy a quantitative method is also of interest.
6. Notes on my personal contribution to papers


   I constructed and characterized all the multilayers used in this work excepts multilayer a in fig. 1 and I participated in the XPS measurements and the analysis of the results. I took part in the development of the first draft and the final form of the paper.


   I planned and carried out most of the experiments described in this paper. I synthesized all the samples used in the research and carried out the ellipsometry and the contact angle measurements as well as most of the AFM characterization (except for the force measurements). I participated in the XPS measurements and analysis of the results. I wrote the first draft of the paper and participated in the development of its final form.


   I participated in the planning and carried out all the experiments and measurements except the HR-SEM imaging, which was performed by Dr. Z. Barkay of Tel-Aviv University. I carried out the analysis of the results, wrote the first draft of the paper and participated in the development of its final form.


   I prepared the gold islands films as well as constructed the multilayers on the islands. I carried out the UV/Vis measurements and the AFM imaging. I performed the analysis of the results, wrote the first draft of the paper and participated in the development of its final form.
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איילנה זזרז - מורה

מוגש لمועצה המ◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌◌昶


T-SPR spectroscopy

inicio mediante