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The heterogeneous growth of P(3MeTh)—an ellipsometric study

L.M. Abrantes [a,b,*], J.P. Correia [b,c], G. Jin [d]

[a] *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisbon, Portugal*

[b] *ICAT, Laboratório de Processos Electroquímicos, Campo Grande, 1749-016 Lisbon, Portugal*

[c] *INETI, Departamento de Energias Renováveis, 1649-038 Lisbon, Portugal*

[d] *Institute of Mechanics, Chinese Academy of Sciences, 15, Zhong-Guan-Cun Road, Beijing 100080, People's Republic of China*

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Abstract

Successive thicker P(3MeTh) layers are analysed by ex situ conventional and imaging ellipsometry. Thin films display a smooth surface, are compact and homogeneous while for a growth charge above 20 mC cm^{-2} the polymer structure modifies to a still uniform but less dense layer. A two-layer model is used and a mathematical procedure is developed to obtain, simultaneously, from the experimental ellipsometric parameters, Δ and Ψ, the thickness and the complex refractive index of P(3MeTh) films grown up to 80 mC cm^{-2}. Thicker polymer layers are disordered and present a high degree of surface roughness.

Keywords: Ellipsometry; Imaging ellipsometry; Refractive index; Poly(3-methylthiophene); Polymer structure

1. Introduction

The electropolymerisation method is recognised as an attractive route for the preparation of conductive polymer layers on electrode surfaces but the information provided by the classical electrochemical techniques must be combined with other measurements for the characterisation of the deposited materials.

It has been shown [1–3] that the synthesis conditions (kind and concentration of electrolyte and solvent nature) as well as electrochemical parameters (applied potential/current, deposition time) critically affect, not only the process efficiency but also the physicochemical properties of the polymer films, namely the morphology, electroactivity, switching times and stability.

In the case of the electrochemical polymerisation of thiophene and its derivatives, several optical methods have been successfully employed to increase the knowledge on the process occurring during film formation and their relationship with polymer performance [4–6]. Recent advances and an increasing interest in utilisation is receiving ellipsometry, a particularly suited tool to obtain information on film thickness and heterogeneity [7–10].

Ellipsometry is a conventional optical technique in which the change of the polarisation state of specularly reflected light from a sample surface, compared with the incident state, is analysed [11]. Since the polarisation state of such reflected light is modulated by the surface under observation, changes in the sample can be monitored. The method is sensitive to modifications of both the amplitude and the phase of the probe light, which can be measured with very high precision. Thus it is an ideal route to investigate small variations on the

* Corresponding author. Tel.: +351-21-7500016; fax: +351-21-7500115.

E-mail address: luisa.abrantes@cd.fc.ul.pt (L.M. Abrantes).

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sample properties such as layer thickness and refractive index even to a sub-monolayer level.

Ellipsometry has been employed for the study of the poly(3-methylthiophene) (P(3MeTh)) electropolymerisation process; it has been possible to discriminate the initial steps of deposition and its dependence on the electrochemical mode and conditions selected for the synthesis [12]. The results from monitoring the evolution of the polymer film optical parameters have also given sound indications on structural modifications upon thickening [13] which have been further supported by atomic force microscopy investigations [14].

From the ellipsometric data on the growth and subsequent oxidation/reduction processes of P(3MeTh) reported so far [12–17] it appears that after a critical thickness there is a significant change in the polymer optical properties due to the formation of a less compact optical structure.

The useful approach of combining ellipsometry and electrochemical measurements has been followed in the present work to characterise P(3MeTh) films from 20 to few hundreds of nanometers, electrodeposited under galvanostatic and potentiostatic control on gold substrates. Conventional ellipsometry was employed in constant wavelength mode to collect the film optical properties at different stages of growth and the dependence of these parameters on the redox state. Additional information on spatial distribution of the polymer layers was obtained by imaging ellipsometry [18]. The results clearly indicate the dependence of P(3MeTh) final properties on the electrosynthesis conditions and significant morphology differences for layers of distinct thickness.

2. Experimental

With the exception of the acetonitrile, which was distilled under argon atmosphere prior to use, all the electrolyte solutions were prepared from 'Analar' grade chemicals as received. They were thoroughly deoxygenated directly in the cell with argon (purity > 99.9997%) and an inert atmosphere was kept over the solution surface during the measurements. All experiments were performed at room temperature (23–24 °C).

A three-electrode cell was employed to perform the electrochemical experiments being the working electrode potential controlled with respect to the saturated calomel electrode (SCE). The working electrodes consist of gold evaporated chromium coated silicon slides (Si, SiO_2 (2 nm), Cr (2 nm), Au (100 nm)) and a large area platinum foil was used as counter electrode.

Poly(3-methylthiophene) films were synthesised from a solution containing 3-MeTh 0.02 mol dm^{-3} and $LiClO_4$ 0.10 mol dm^{-3} in acetonitrile. The electropolymerisation was carried out under potentiostatic (E_g = 1.50, 1.56 V) or galvanostatic ($i_g = 2$ mA cm^{-2}) control and the growth charge 20 and 120 mC cm^{-2}. A stepped sample with 20, 40, 59 and 78 mC cm^{-2} growth charge was also prepared at $E_g = 1.56$ V. A Teflon tape was used to delimit the electrode areas to be covered by the polymer layers.

The film redox behaviour was examined, in a monomer-free solution, by cycling the potential between 0 and 1 V at 50 mV s^{-1}. After the electrochemical characterisation, the electrodes were thoroughly rinsed with acetonitrile and 'dried' by a flux of argon (to remove the excess of CH_3CN from the electrode) and measured thereafter; in this way, the polymer keeps a 'wet' condition similar to that in the solution.

Ex situ optical characterisation of P(3MeTh) films was carried out in an ellipsometer of rotating analyser type (SE 400, SENTECH, Germany) equipped with a He–Ne laser ($\lambda = 632.8$ nm), at 70° incident angle.

A home-made ellipsometric imaging system [18] was used for the visualisation of polymer layers. The basic experimental set-up was a conventional PCSA optical system, consisting of polariser, compensator, sample, and analyser, combined with a charge-coupled device (CCD) camera instead of the traditional photo-detectors with the performance of simultaneous null and off-null ellipsometry. In order to visualise a large area of sample surface, an expanded probe beam was used to replace the narrow beam in a conventional ellipsometer. It consisted of a Xenon lamp and a specific collimating system to provide an expanded parallel probe beam with a diameter of about 40 mm. The beam going out of the collimating system passed through a polariser and a compensator (a quarter wave plate) and finally onto the sample at a given incident angle. A 633 nm interference filter was placed in the incident optical path to increase the ellipsometric contrast of image. The reflected beam passed through an analyser and an imaging lens with a spatial filter, and then the ellipsometric image of the surface was captured with a CCD camera controlled by an auto-focusing system. An analog picture, converted to a digital one in greyscale format (10 bits, 0–1023 greyscale), was stored in a computer for further evaluation by an image processing program.

In real operation, the ellipsometric null condition was set on the bare surface of the substrate. The relative intensity distribution in the field of view was sufficient to show the thickness distribution of the layers.

The measure of an absolute thickness of a thin layer was performed by conventional ellipsometry (refractive index of the substrate: $\tilde{n} = 0.22–0.333i$; $\Psi = 43.313$, $\Delta = 106.687$), and the relative thickness distribution visualised with the imaging ellipsometry. The thickness accuracy of the imaging system was better than 0.3 nm, with 3 μm for a lateral resolution.

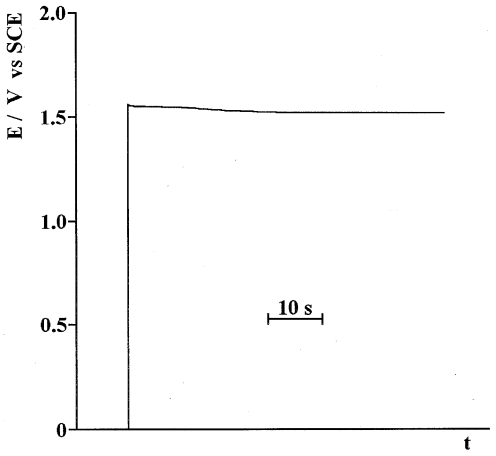

Fig. 1. Potential profile of the galvanostatic polymerisation of 3MeTh at $i_g = 2$ mA cm^{-2}.

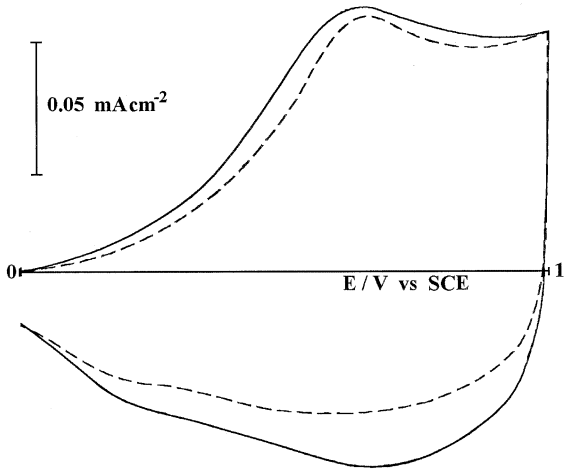

Fig. 2. Comparison of the redox behaviour of P(3MeTh) films ($Q_g = 20$ mC cm^{-2}) grown under potentiostatic (—) and galvanostatic control (- - -). $v = 50$ mV s^{-1}.

3. Results and discussion

A systematic study on the potentiostatic polymerisation of P(3MeTh) films on gold [19] have shown that the rate of growth changes significantly with a slight difference in the applied potential; on the other hand, under 2 mA cm^{-2} controlled current, the polymer build-up occurs at a fairly constant potential, little above 1.5 V (1.55 V, $t_g = 10$ s; 1.52 V, $t_g = 60$ s) — Fig. 1. In both cases the potential of growth is beyond the value required for the polymer doping and thereafter P(3MeTh) layers as-prepared will be designated 'oxidised' whereas the term 'reduced' stands for films removed from the electrolyte solution after being subjected to 0.0 V for 12 min.

Table 1 contrasts the ellipsometric parameters Δ and Ψ recorded for P(3MeTh) prepared under different electrochemical conditions using 20 and 120 mC cm^{-2} growth charge. At each growth condition, the values of Δ and Ψ show the changes in optical properties brought about by the oxidation and reduction of P(3MeTh) films. Taking into account that the phase parameter is only slightly dependent on the absorption modes of the polymer, the increase in Δ values from reduced to oxidised states must be ascribed to a polymer thickness modification upon doping, phenomena which has also been reported for other systems [20,21].

For thin layers ($Q_g = 20$ mC cm^{-2}) there is a regular variation of Δ and Ψ with the rate of polymerisation but the change in the phase parameter is marked and shall be related with the polymer arrangement dependence on the growth conditions—less regular distribution as the rate of deposition increases. The azimuth, as an amplitude parameter, strongly depends on the energy loss of the light caused by the interaction with the film, and then, responds mainly to the population of energy levels present in the polymer. So, the differences in Ψ observed for the polymers in the reduced state, should be attributed to a distinct ability of the films to carry out the undoping process completely. It is interesting to note that the change of the Ψ value of the galvanostatically grown film from the reduced to the oxidised state is quite low revealing poor electroactivity of the polymer. Indeed, the comparison of the redox behaviour of polymers grown under galvanostatic and potentiostatic control (Fig. 2) also reveals a lower electrochemical reversibility of the film prepared at constant current ($(Q_{ox}/Q_{red})^{i_g} = 1.24$, $(Q_{ox}/Q_{red})^{E_g} = 1.10$).

Table 1
Ellipsometric parameters of the P(3MeTh) films

Growth conditions	$Q_g = 20$ mC cm^{-2} (ψ, Δ)		$Q_g = 120$ mC cm^{-2} (ψ, Δ)	
	Reduced	Oxidised	Reduced	Oxidised
$E_g = 1.50$ V	43.52, 78.19	41.85, 83.43	40.95, 256.01	46.96, 297.45
$E_g = 1.56$ V	43.00, 86.23			
$i_g = 2.0$ mA cm^{-2}	42.78, 88.65	41.67, 89.09	40.64, 246.88	76.35, 294.88

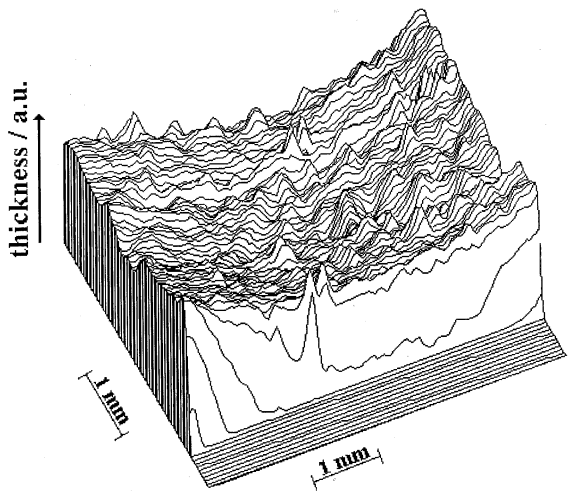

Fig. 3. Thickness distribution of a P(3MeTh) film in the reduced state. $E_g = 1.50$ V; $Q_g = 120$ mC cm^{-2}. 25–30 μm lateral resolution.

The differences in the corresponding values of Δ and Ψ, caused by altering the electropolymerisation route, are quite distinct for thin (20 mC cm^{-2}) and thick (120 mC cm^{-2}) layers. The dispersion of ellipsometric parameters observed in the later case reflects a non-uniform thickness increase, which was also confirmed by imaging ellipsometry (Fig. 3). Since for a given wavelength and angle of incidence, Δ and Ψ are a function of the complex refractive index and thickness of the film, no effort is made in the present work to deduce optical parameters for such thick polymers.

Conventional ellipsometry is limited to the normal two-parameters measurements (Δ, Ψ) and to characterise any film by the refractive index, n, and the extinction coefficient, k, at least three experimental parameters are needed. The usual approach is to estimate the thickness of the layer using a suitable model [22,23]. For P(3MeTh) and $Q_g = 20$ mC cm^{-2}, unambiguous literature information support the assumption of polymer homogeneous growth; the film thickness L_f, can thus be estimated by the linear relationship

L_f (nm) = αQ_g (mC cm^{-2}).

The α parameter is known to depend on the working conditions [17] being reported values between 1 and 10 [24–28]. In the present work, calculated values of n and k parameters in very good agreement with those published for the same polymer [14,17] dictated the choice of $\alpha = 1$.

Table 2 presents the calculated refractive indexes and extinction coefficients, illustrating the influence of the electrochemical mode employed for P(3MeTh) preparation and the dependence on the polymer growth potential and on its state of oxidation. For the reduced form, a decrease in the refractive index is observed as the polymer synthesis potential becomes more anodic, indicating that a faster deposition process produces a less ordered layer. The n values for oxidised and reduced forms ($\alpha = 1$) also reflect the transition between a compact and a less dense material upon doping; the correspondent polymer swelling is not so marked for films galvanostatically prepared, likely due to its less compact and lower ordered nature. It is worthwhile to note that a 10% increase in thickness promoted by the polymer oxidation leads to calculated values of n and k ($\alpha = 1.1$) presenting the same trends.

The extinction coefficients observed for the oxidised form of the polymers prepared under different rates of growth can be directly correlated with electronic structures induced by the growth conditions. A lower number of polaronic/bipolaronic states (lower conductivity) shall be expected in P(3MeTh) layers synthesised at high potentials. This behaviour suggests that a high rate of polymerisation promotes the formation of branched structures where the oxidation process occurs to a lesser extent.

In an attempt to further characterise the polymer formation, namely a uniform and homogeneous thin film developing into a porous polymer layer with the growing process, a two-layer model was used consisting of a thick porous polymer on the top of a compact thin film ($L_f = 20$ nm) on a known substrate. The system is characterised by six parameters, n_r, k_r and L_r for the top porous layer and n_h, k_h and L_h for the thin uniform one. The above-described methodology ($\alpha_h = 1$) was followed to compute the optical parameters of the

Table 2
Refractive indexes (n) and extinction coefficients (k) of P(3MeTh) films grown with $Q_g = 20$ mC cm^{-2}

Growth conditions	n		k	
	Reduced ($\alpha = 1.0$)	Oxidised ($\alpha = 1.0$, 1.1)	Reduced ($\alpha = 1.0$)	Oxidised ($\alpha = 1.0$, 1.1)
$E_g = 1.50$V	2.103	1.732, 1.639	0.049	0.229, 0.206
$E_g = 1.56$ V	1.625		0.083	
$i_g = 2.0$ mA cm^{-2}	1.500	1.458, 1.403	0.092	0.192, 0.167

Table 3
Ellipsometric parameters of P(3MeTh) films (reduced state) grown at $E_g = 1.56$ V

Q_g (mC cm^{-2})	ψ	Δ
39.5	44.14	78.52
58.9	46.89	76.82
78.0	56.77	85.91

bottom polymer layer and $n_h = 1.625$, $k_h = 0.083$, $L_h =$ 20 nm could be deduced from the ellipsometric parameters Ψ and Δ with a single layer model. The top porous layer is expected to be less ordered and then α will be far from 1, and cannot be simply assumed. To overcome the difficulty in deducing three unknown parameters (n_r, k_r and L_r) from two experimental measurements (Δ, Ψ), two thick polymer layers were prepared under a charge fairly larger than 20 mC cm^{-2}, and the respective ellipsometric parameters determined: Ψ_1, Δ_1 ($Q_g = 59$ mC cm^{-2}) and Ψ_2, Δ_2 ($Q_g = 78$ mC cm^{-2}) — Table 3.

The two samples were treated by the two-layer model and therefore, in spite of the difference in thickness, the structure of both layers must be assumed to be consistent, which means that the complex refractive index ($n - ik$) shall be the same. This being so the number of rest unknowns for both samples is four (n_r, k_r, L_{r1} and L_{r2}) which can be deduced from the four experimental measurements (Ψ_1, Δ_1, Ψ_2, Δ_2). As depicted in Fig. 4, a series of thickness values has been introduced into the two-layer model to deduce n and k values from Ψ_1 and Δ_1 and the method repeated to obtain another series of n and k from Ψ_2 and Δ_2. When the values in the two series of n and k are convergent in the n–k coordinates (Fig. 4) the value of $(1.299 - i0.120)$ at the cross point of the two curves is the refractive index ($n_r - ik_r$) of the porous layer. The corresponding thickness values for both porous top layers are 68 and 94 nm for $Q_g = 59$ and 78 mC cm^{-2}, respectively. The total thickness of the two samples is 88 and 114 nm ($L_f = \alpha_h L_h + \alpha_r L_r$). It is interesting to note that α_r takes a value of 1.6–1.7 for polymer layer formation under this condition of growth.

Fig. 5 shows the surface profile of P(3MeTh) stepped layers on gold, prepared under 20, 40, 59 and 78 mC cm^{-2}, obtained by imaging ellipsometry. Since the thickest part of the sample was out of the dynamic range of imaging, the visualisation has been performed step by step, keeping the same measurement conditions and unit for the thickness, from the substrate to the first layer and from this to the second one and so on. Finally, all images were integrated. As can be seen in Fig. 5, thin layers show little surface roughness but for Q_g over 40 mC cm^{-2} the lack of uniformity is apparent and for $Q_g = 78$ mC cm^{-2} the porous, disordered state of the polymer is evident. Also presented in this figure is the estimated thickness of the polymer layers (in arbitrary units), computed by geometric evaluation of the image, assigning a thickness of 20 to the first one.

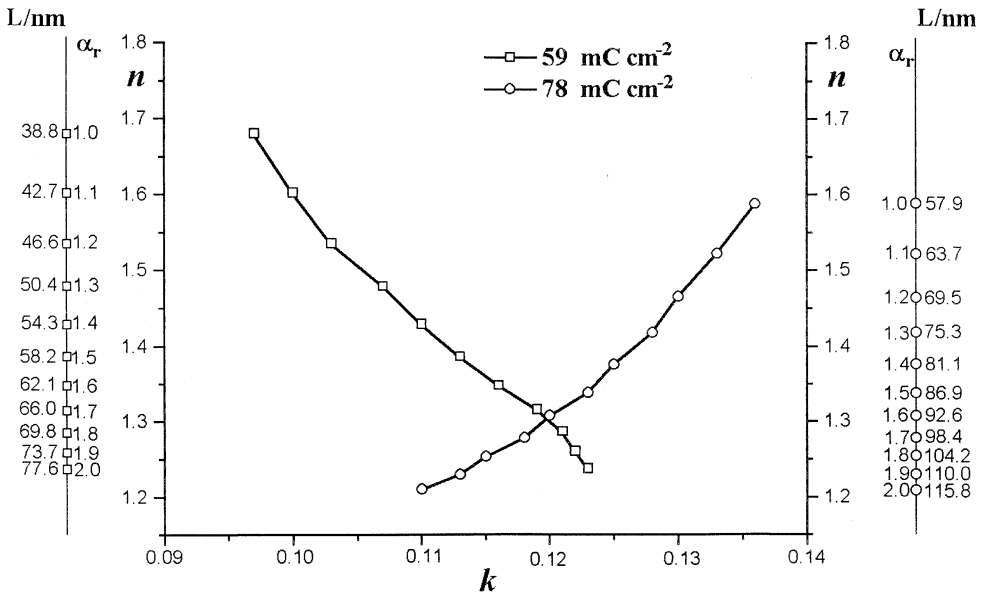

Fig. 4. The evaluation for the n, k and thickness for the porous layer in thick P(3MeTh) films, $E_g = 1.56$ V; reduced state.

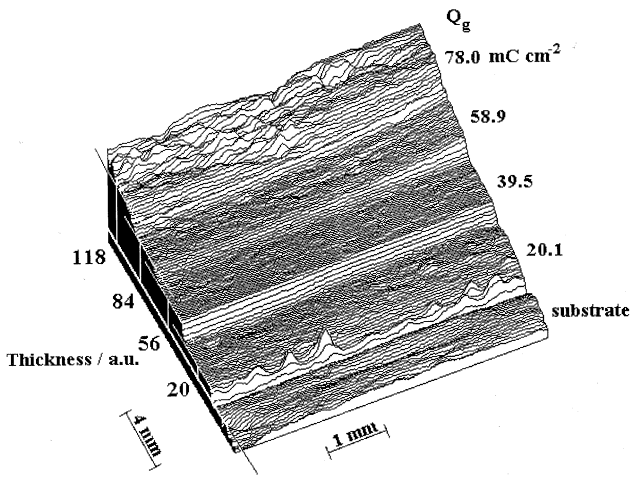

Fig. 5. A profile of a stepped sample of P(3MeTh) visualised with imaging ellipsometry. Films grown with $Q_g = 20$, 40, 59, and 78 mC cm^{-2}. 25–30 μm lateral resolution.

Although any absolute value for the layer thickness can be taken from the imaging ellipsometry, the data strongly support the above described procedure in spite of using only two Ψ/Δ points to characterise each layer in the stepped sample. About the same step in the growth charge has been used to prepare the layered sample and there is a much more marked relative increase in the thickness from the first to the second layer than for the polymer thickening thereafter.

This approach does not reveal the step in the film optical density (previously reported [12,13]) but gives a reasonable basis to assume that on the top of a first compact uniform film, the electropolymerisation process may involve, e.g. for growth charges higher than 20 mC cm^{-2} ($E_g = 1.56$ V) the formation of a second layer displaying different properties. It must be pointed out that even a porous polymer can display a smooth surface, namely at the beginning of its formation. It is likely that the disorder and porosity increases for very thick films; irrespective to the thickness, a very high growth charge (e.g. $Q_g = 120$ mC cm^{-2}) will originate highly branched porous polymer films.

4. Conclusions

Analysis of ex situ ellipsometric data allows the description of several stages during the electrodeposition of P(3MeTh) on gold and to explain the modification of polymer properties with thickness.

Two different polymer layers are successively formed on the electrode surface and a two-layer model can describe the system. A thin ordered and homogeneous film is formed up to about 20 nm (being the thickness equivalent to the charge consumed in polymer deposition); this layer is progressively modified into a less dense film.

The thickness of the top layer can be estimated using a mathematical procedure where the film structure is considered similar for growth charges from 20 to 80 mC cm^{-2}. For greater polymerisation charges the polymer is disordered, its porosity increases and the surface organisation is lost.

P(3MeTh) layers at several stages of the electrodeposition process are thus expected to exhibit different concentration and distribution of active redox centres. Further work is in progress for the comparison of P(3MeTh) film characteristics combining ellipsometric and electrochemical information.

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