



HAL
open science

Rapid ellipsometric determination and mapping of alloy stoichiometry with a neural network

Y. Battie, Adrià Canós Valero, David Horwat, Aotmane En Naciri

► To cite this version:

Y. Battie, Adrià Canós Valero, David Horwat, Aotmane En Naciri. Rapid ellipsometric determination and mapping of alloy stoichiometry with a neural network. *Optics Letters*, 2022, 47 (8), pp.2117-2120. 10.1364/OL.457147 . hal-04053491

HAL Id: hal-04053491

<https://hal.science/hal-04053491>

Submitted on 31 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Rapid ellipsometric determination and mapping of alloy stoichiometry with a neural network

A YANN BATTIE,^{1,*} ADRIA CANOS VALERO,² DAVID HORWAT,² AOTMANE EN NACIRI¹

¹Université de Lorraine, Laboratoire de Chimie et Physique, Approche Multiéchelle des Milieux Complexes (LCP-A2MC), 1 Bd Arago, 57070 Metz

²Université de Lorraine, Institut Jean Lamour (IJL, UMR 7198, Campus Artem, 2 allée André Guinier, 54011 Nancy

*Corresponding author: yann.battie@univ-lorraine.fr

Received XX Month XXXX; revised XX Month, XXXX; accepted XX Month XXXX; posted XX Month XXXX (Doc. ID XXXXX); published XX Month XXXX

Due to their tunable physical and chemical properties, alloys have a fundamental importance for material science. The determination stoichiometry is crucial for alloys engineering. Classical characterization tools such as energy-dispersive X-ray spectroscopy (EDX) are time consuming and cannot be performed in ambient atmosphere. In this context, we introduce a new methodology to determine the stoichiometry of alloys from ellipsometric measurements. This approach, based on the analysis of ellipsometric spectra by an artificial neural network (ANN), is applied on electrum alloys. We demonstrate that the accuracy of this approach is in the same order of magnitude as the EDX one. In addition, the ANN analysis is sufficiently robust to be used to characterized rough alloys. Finally, we demonstrate that the exploitation of ellipsometric map with the ANN is a powerful tool to determine composition gradients in alloys.

The ability to control the electronic and/or optical properties through a careful tuning of their stoichiometry renders alloys as attractive materials with significant degrees of freedom for the design of applications in electronics, solar cells or sensors [1-3]. Thus, the determination of their composition is crucial in modern material science. In recent decades, several analytical techniques, such as energy-dispersive X-ray spectroscopy (EDX), or optical emission spectroscopy (OES), have become commercially available, enabling quantitative assessments of alloy compositions. However, these technics require vacuum chamber and cannot be implemented in-line for mass production. Thus, the development of complementary and fast characterization tools is a key point for controlling the alloy stoichiometry after synthesis.

Several works have shown that spectroscopic ellipsometry is sensitive to the material composition [4-13]. For instance, the volume fraction of nanoparticles in a matrix can be deduced from ellipsometric measurements [4]. Ellipsometry has also been used to determine the complex dielectric functions of several alloys [6-13]. The parameters of the dispersion law used to analyze ellipsometric spectra are directly linked to the stoichiometry. Peña-Rodríguez et al. have shown that the damping parameter of free electrons in Au_xAg_{1-x} alloys, estimated from ellipsometry, exhibits a quadratic dependence with the stoichiometry [6]. In the case of semiconducting alloys, several authors have correlated the stoichiometry to the gap energy or to the energy of optical transitions found by ellipsometry [8-13]. Despite ellipsometry can provide some significant insights concerning the composition of materials, the analysis of ellipsometric spectra requires a modeling step based on several assumptions. Namely, a suitable dispersion law capable of adequately reproducing the optical properties of the alloy for all compositions must be selected a priori. The development of artificial intelligence offers exciting new pathways to overcome this bottleneck. However, recent works combining

ellipsometry and an artificial neural network (ANN) analysis only focused on the determination of the dielectric function of materials [14-15] or the characterization of the profile of diffraction gratings [16-17].

The aim of this letter is to demonstrate that ellipsometric measurements together with a neural treatment can lead to an accurate and reliable determination of an alloy stoichiometry. This proof of concept is performed on electrum (Au_xAg_{1-x}) alloys since the Au–Ag system has great potential for plasmonic applications and forms a totally miscible alloy in the solid phase according to the Hume–Rothery rules.

1. Materials and methods

Two Au_xAg_{1-x} alloy films with lateral composition gradients, labelled sample 1 and sample 2, were deposited at room temperature on clean glass substrate by using direct current magnetron sputtering of Au and a Ag targets (2 in. diameter, 3 mm thickness, and 99.99 at.% purity 99.9%) simultaneously sputtered in argon at a pressure of 0.3 Pa. The film thickness is about 450 nm. The targets were placed vertical and parallel and their axes were separated by a distance of 14 cm. The substrates were placed parallel to the target surfaces and along the line joining the target axes. The distance separating the surface of the targets and the surface of the substrates was fixed at 10 cm. The discharge currents applied to the gold and silver targets were $I_{Au} = 67$ mA and $I_{Ag} = 50$ mA in order to compensate the difference in sputtering yields, $Y_{Au} = 2.43$ and $Y_{Ag} = 3.4$, between the two metals. The co-deposition of two materials from individual sources spatially separated on a static substrate holder is a combinatorial approach generating spatial variation of the chemical composition and can be usefully applied to screen alloy properties [18]. In the present case, both metals generate an Au_xAg_{1-x} alloy with a stoichiometry gradient (x). To understand this, it is necessary to consider that the sputtered flux

decreases as particles are sputtered off the target axes along a line of sight making an increasing angle α from the target axes (for data on Au and Ag see reference [19]) and also that the distance between the center of a target and a substrate increases with α . Consequently, the flux from deposited from a sputtered target decreases with α .

The composition of the alloy films was first characterized by means of EDX measurements directly performed in a scanning electron microscope (Philips XL30S FEG) and taking into account AgL and AuM transitions. The energy spectra of X-Ray scattering at each position in the sample was recorded with a secondary detector after irradiation with a LaB6 source of primary electrons accelerated under 10 kV. The spectra were then fitted considering the Phi-Rho-Z method using tabulated data for Au and Ag in order to accurately determine the concentration of each element.

Ellipsometry is an indirect characterization tool which measures the changes of the polarization state between the incident and the reflected light on the samples. The measured values are the ellipsometric angles (ψ, Δ) related to the ratio of the Fresnel amplitude reflection coefficients of the sample:

$$\tan \psi e^{j\Delta} = \frac{r_p}{r_s}. \quad (1)$$

r_p and r_s are reflection coefficients of the sample for p-polarized and s-polarized light, respectively. The ellipsometric spectra are recorded every 5 nm from 270 nm to 700 nm with an UVISSEL Horiba Jobin Yvon ellipsometer. The angle of incidence was set to 70°. The high accuracy mode was used to measure the ellipsometric angles ψ and Δ .

2. Results and discussion

To determine the alloy stoichiometry from ellipsometric spectra, we implemented an ANN which has a multilayer perceptron architecture (Figure 1). It consists of an input vector, a hidden layer, and an output layer. The input vector contains the ellipsometric angles ψ and Δ , while the hidden and output layers are composed of mathematical units called neurons. In the following, the number of hidden neurons is arbitrarily set to 10. The output layer only contains one neuron. The layers are linked together by weighted synaptic connections. Each neuron m applies a specific transfer function g to its weighted inputs:

$$o_m = g\left(\sum_{p=0}^P w_{m,p} x_p\right). \quad (2)$$

$w_{m,p}$ is the synaptic weight between the input x_p and the neuron m . The transfer functions of the hidden neurons and output neurons are sigmoid and linear functions, respectively. According to Cybenko, this ANN architecture is a universal approximator [20]. Indeed, it can approximate any function with a finite number of discontinuities. Once the neural network is designed, it should be trained to learn the relationship between its inputs and output. This step requires input/output data. The input data corresponds to the ellipsometric angles measured by ellipsometry on sample 1. The output data are the corresponding stoichiometry determined by EDX. 30 couples of input/output data recorded. These couples of data are then split into 20 pairs of training data, 5 pairs of validation data and 5 pairs of test data. The synaptic weights were then adjusted by using the back propagation Levenberg-Marquardt

algorithm to minimize the root mean square error (rmse) between the training data and the ANN response. To prevent overlearning, the training stage is stopped by using the early stopping method, i.e. when the root-mean-square error evaluated from validation data increases.

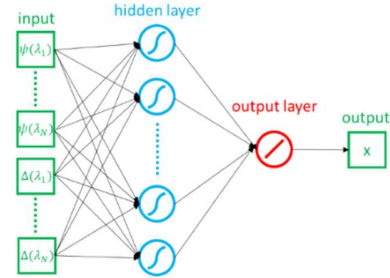


Fig. 1. Structure of the ANN used in this work. The ANN contains one hidden layer composed of 10 neurons with sigmoidal transfer function. The output layer contains 1 neuron with linear transfer function. The ANN inputs are the ellipsometric angle ψ and Δ measured in the 270 nm-700 nm spectral range by steps of 5 nm. The ANN output is the stoichiometry x of $\text{Au}_x\text{Ag}_{1-x}$ alloy.

The ANN performance, is quantified by calculating the relative error between the stoichiometry values obtained by EDX and the ANN. The relative errors on the stoichiometry evaluated from the training, validation and test data are smaller than 0.07%. This value is negligible compared to the relative error of EDX measurements, estimated to 5%. We conclude that even for a small number of training samples, the accuracy of our technique is only limited by the accuracy of the EDX measurement used to build the training data.

Since ellipsometry is also sensitive to the surface roughness, we estimated the impact of roughness on the stoichiometry value. First, we recorded an ellipsometric spectrum performed at an arbitrary position on sample 1. By considering the film as a semi-infinite isotropic medium, we analytically determined the complex dielectric function of this alloy (ϵ_{alloy}) from ellipsometric measurements [21]. Then, a model was built to simulate the ellipsometric spectra of the roughened alloy. This model is composed of an alloy substrate, with dielectric function ϵ_{alloy} , covered by a layer of thickness (h) composed of a mixture of alloy and vacuum. The dielectric function of the layer is described by the Bruggeman effective medium theory [21]. We assume that the volume fraction of alloy in the roughness layer is equal to 50%. The simulated spectra were used as new input of the ANN. Then, we calculated the relative error on stoichiometry induced by the roughness as follows:

$$\frac{\Delta x}{x} = 100 \left| \frac{x(h) - x(0)}{x(0)} \right|. \quad (3)$$

As shown in Figure 2, the relative error on stoichiometry remains smaller than 5% for $h < 25$ nm, while it drastically increases for a higher thickness value. Despite ellipsometry is sensitive to the surface roughness, it can be concluded that the ANN analysis is sufficiently robust to evaluate the stoichiometry of alloys having a roughness layer not thicker than 25 nm. This limit could be improved by training the ANN with data obtained on rough

samples. However, the latter is beyond the scope of the paper and is left for a future work.

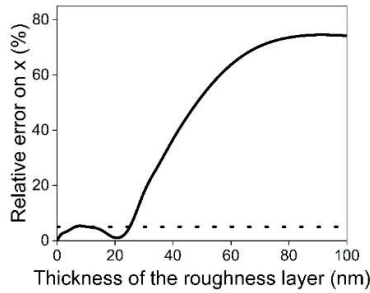


Fig. 2. Evolution of the relative error on stoichiometry as function of the thickness of the alloy roughness layer. The dashed line corresponds to a relative error of 5%.

To validate our approach, ellipsometric measurements recorded on sample 2 were used as new ANN input. Figure 3 compares the stoichiometry estimated from the neural analysis of ellipsometric spectra with those determined by EDX. Both techniques yield similar stoichiometry values. Thus, ellipsometric spectra can be considered as a fingerprint of the alloy composition.

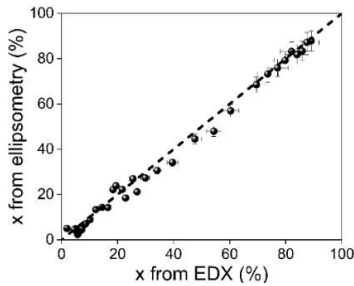


Fig. 3. Comparison between the stoichiometries determined by ellipsometry ($x_{\text{ellipsometry}}$) and EDX (x_{EDX}). The dashed line stands for $x_{\text{ellipsometry}} = x_{\text{EDX}}$. The error bars are obtained by considering a relative error of 5% on the stoichiometry values.

Ellipsometry can also be used to investigate the optical of materials. Each measured spectrum can be modeled to evaluate the complex dielectric function of alloys. The model used consists in an alloy substrate covered with a roughness layer with a thickness h . The dielectric function used to model the optical properties of the alloys is the sum of two terms [22]. The first term modeled by a Drude law describes the intraband transitions of free electrons of the alloy. The second term modeled by a Tauc-Lorentz law with 3 oscillators describes the intraband transitions. Figure 4 shows the measured dielectric function for 5 stoichiometries estimated from ellipsometry. The real part of the dielectric function of alloys is negative in the visible spectral range confirming that $\text{Au}_x\text{Ag}_{1-x}$ alloys have metallic behavior. For wavelength smaller than 550 nm, the imaginary part of the dielectric function of alloys lies between those of silver and gold. The interband transition threshold is progressively redshifted as the stoichiometry increases. This behavior which was previously observed by several authors [6-7], is a characteristic of solid solutions. In contrast, the variations of the

imaginary part of the dielectric function are not monotonous at higher wavelength than 550 nm. Indeed, its amplitude reach a maximum for a stoichiometry value located in the 29%-50% range. In this spectral range, the imaginary part of the dielectric function is inversely proportional to the mean free path of the conduction electrons. Since alloys are disordered materials, the random distribution of Au and Ag atoms in the crystal lattice of alloys destroys the periodicity of the structure and reduces the mean free path of free electrons. These results also suggest that the dielectric function of alloys is not a composition-weighted average of the dielectric function of gold and silver.

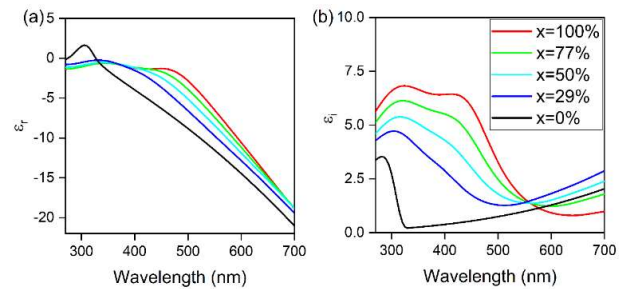


Fig. 4. (a) real part and (b) imaginary part of the dielectric function of $\text{Au}_x\text{Ag}_{1-x}$ alloys measured by ellipsometry for 5 stoichiometries. The stoichiometries are determined from ellipsometry.

Thus, the exploitation ellipsometric spectra with an ANN provides the same insight on the stoichiometry as EDX. However, ellipsometry has several advantages: i) The ellipsometer is less expensive than EDX facilities ii) ellipsometry and the ANN analysis are compatible with in-situ and real time characterizations. As example, ellipsometric spectra with a sampling time of 25 ms can be recorded by using a charge coupled device (CCD) sensor as detector [23]. The ANN analysis of a spectra takes approximately 14 ms. Thus, the stoichiometry of alloys can be estimated in 40 ms. However, to improve the signal to noise ratio, several spectra are often averaged and the measurements of the stoichiometry can take few hundred of ms. In addition, by considering recent development in imaging ellipsometry [24], ellipsometric map can be achieved without moving the sample. iii) Ellipsometry can be used to simultaneously determine the stoichiometry and the dielectric function of alloys, iiiii) ellipsometry can provide information on the extreme surface of alloys. Indeed, depth resolution of ellipsometry is given by the penetration depth of light estimated to few tens of nanometer for Au and Ag. On the contrary, EDX depth resolution is limited to a few micrometers by the penetration and spreading of the electron beam. iiiiii) Contrary to EDX, ellipsometry does not require a vacuum environment and can directly work in ambient atmosphere.

We now explore the opportunity to use ellipsometry to estimate the stoichiometry gradient of alloys. Ellipsometric mapping is performed on sample 2 with a focused spot of 150 μm . 165 spectra were recorded with a step of 0.6 mm along the sample length and 1.5 mm along the sample width. Each spectrum was analyzed with the ANN. For a 1.6 GHz Intel Core processing unit, only 2.4 s are required to analyze all spectra. Figure 5 shows the corresponding stoichiometry map. Along the gradient direction, the stoichiometry progressively varies from 100% (pure gold) to 0% (pure silver). On

the other end, the stoichiometry is almost constant in the direction perpendicular to the gradient. This result is in accordance with the set-up architecture used for the elaboration of alloys. Effectively, in absence of collisions between sputtered particles and argon atoms from the background gas during their drift from the target to the substrate, one would observe a concentric decrease of the deposited flux from the intersection point between a target axis and the substrate. Yet, this is mitigated by the interference between the two sources and, since the mean free path for collisions is in the order of 2 cm, by collisions as particles drift from the target towards the substrate. This result confirms that ellipsometry, combined with an ANN analysis, can be used to evaluate the spatial inhomogeneities of alloy stoichiometry.

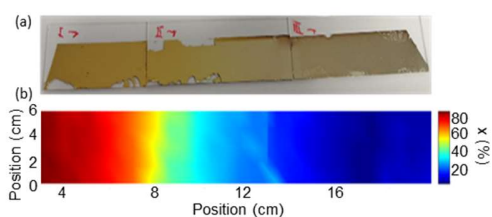


Fig. 5. (a) Picture of sample 2. (b) Stoichiometry map of sample 2 determined by spectroscopic ellipsometry.

In this letter, a neural network analysis is introduced to evaluate the composition of Au_xAg_{1-x} alloys from ellipsometric spectra. The stoichiometry data obtained from ellipsometry is in accordance with those determined by EDX. The accuracy of our technique is in the same order of magnitude as the accuracy of EDX. We have also demonstrated the robustness of ANN for measurements on alloys with surface roughness smaller than 25 nm. While the approach has only been tested on Au_xAg_{1-x} alloys, it can be straightforwardly generalized to other alloys such as semiconducting alloys or ternary alloys. In this case, a new training set is required for each alloy.

Acknowledgments. We thank the Ellipsometry core facility of LCP-A2MC (université de Lorraine, <http://lcp-a2mc.univ-lorraine.fr>).

Disclosures. The authors declare no conflicts of interest.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

References

- H. Yeon, P. Lin, C. Choi, S. H. Tan, Y. Park, D. Lee, J. Lee, F. Xu, B. Gao, H. Wu, H. Qian, Y. Nie, S. Kim, and J. Kim, Alloying conducting channels for reliable neuromorphic computing, *Nat. Nanotechnol.* **15**, 574-579 (2020).
- J. D. Poplowsky, W. Guo, N. Paudel, A. Ng, K. More, D. Leonard, and Y. Yan, Structural and composition dependence of the $CdTe_{1-x}Se_x$ alloy layer photoactivity in $CdTe$ -based solar cells, *Nat. Commun.* **7**, 12537 (2016).
- A. H. Jones, S. D. March, S. R. Bank, and J. C. Campbell, Low-noise high-temperature $AlInAsSb/GaSb$ avalanche photodiode for 2- μm applications, *Nat. Photon.* **14**, 559-563 (2020).
- Y. Battie, A. En Naciri, N. Chaoui, Y. Le Gall, D. Muller, M. Carrada, and D. Mathiot, Plasmonic properties of implanted Ag nanoparticles in SiO_2 thin layer by spectroscopic ellipsometry, *J. Appl. Phys.* **122**, 085308 (2017).
- J. Song, H. Li, J. Li, S. Wang, and S. Zhou, Fabrication and optical properties of metastable Cu-Ag alloys, *Appl. Opt.* **41**, 5413 (2002).
- D. Rioux, S. Vallières, S. Besner, P. Muñoz, E. Mazur, and M. Meunier, An analytic model for the dielectric function of Au, Ag, and their alloys, *Adv. Optical Mater.* **2**, 176-182 (2014).
- O. Peña-Rodríguez, M. Caro, A. Rivera, J. Olivares, J. M. Perlado, and A. Caro, Optical properties of Au-Ag alloys: An ellipsometric study, *Opt. Mater. Express* **4**, 403-410 (2014).
- P. Narang, S. Chen, N. C. Coronel, S. Gul, J. Yano, L.-W. Wang, N. S. Lewis, and H. A. Atwater, Bandgap tunability in $Zn(Sn,Ge)N_2$ semiconductor alloys, *Adv. Mater.* **26**, 1235-1241 (2014).
- W. Limberger, C. C. Mardare, C. Cobet, J. Zuo, A. W. Hassel, and A. I. Mardare, Spectroscopic ellipsometry for compositionally induced bandgap tuning of combinatorial niobium-tantalum anodic oxides, *RSC Adv.* **6**, 79934-79942 (2016).
- B. Kalas, Z. Zolnai, G. Sáfrán, M. Serényi, A. Agocs, T. Lohner, A. Nemeth, N. Quoc Khánh, M. Fried, and P. Petrik, Micro-combinatorial sampling of the optical properties of hydrogenated amorphous $Si_{1-x}Ge_x$ for the entire range of compositions towards a database for optoelectronics, *Sci. Rep.* **10**, 19266 (2020).
- C. Mihai, F. Sava, I. D. Simandan, A. C. Galca, I. Burducea, N. Becherescu, and A. Velea, Structural and optical properties of amorphous Si-Ge-Te thin films prepared by combinatorial sputtering, *Sci. Rep.* **11**, 11755 (2021).
- M. Bouska, V. Nazabal, J. Gutwirth, T. Halenkovic, J. Prikryl, S. Normani, and P. Nemeč, $GaTe-Sb_2Te_3$ thin films phase change characteristics, *Opt. Lett.* **45**, 1067-1070 (2020).
- A. Hazari, A. Bhattacharya, T. Frost, S. Zhao, Md. Zunaid Baten, Z. Mi, and P. Bhattacharya, Optical constants of $In_xGa_{1-x}N$ ($0 \leq x \leq 0.73$) in the visible and near-infrared wavelength regimes, *Opt. Lett.* **14**, 3304-3307 (2015).
- Y. Battie, S. Robert, I. Gereige, D. Jamon, and M. Stchakovsky, Demonstration of the feasibility of a complete ellipsometric characterization method based on an artificial neural network, *Appl. Opt.* **48**, 5318-5323 (2009).
- J. Liu, D. Zhang, D. Yu, M. Ren, and J. Xu, Machine learning powered ellipsometry, *Light: Sci. Appl.* **10**, 1-7 (2021).
- I. Gereige, S. Robert, S. Thiria, F. Badran, G. Granet, and J. J. Rousseau, Recognition of diffraction-grating profile using a neural network classifier in optical scatterometry, *J. Opt. Soc. Am. A* **25**, 1661-1667 (2008).
- Z. S. Fawzi, S. Robert, I. El Kalyoubi, and B. Bayard, Analysis and detection of an incorrect profile shape in a classical scatterometric process, *Eur. Phys. J. Appl. Phys.* **76**, 31001 (2016).
- A. Borroto, S. Bruyère, N. Thurieau, C. Gendarme, E. Jimenez-Piqué, J. J. Roa, J. F. Pierson, F. Mücklich, and D. Horwat, Structural and mechanical properties of $Zr_{1-x}Mo_x$ thin films: From the nano-crystalline to the amorphous state, *J. Alloys and Compd.* **729**, 137-143 (2017).
- Y. V. Martynenko, A. V. Rogova, V. I. Shul'Ga, Angular distribution of atoms during the magnetron sputtering of polycrystalline targets, *Tech. Phys.* **57**, 439-444 (2012).
- G. Cybenko, Approximation by superpositions of a sigmoidal function, *Math. Control Signals Systems* **2**, 303-314 (1989).
- H. Fujiwara, *Spectroscopic ellipsometry: Principles and applications*, (John Wiley & Sons, 2007).
- W. Chamorro, J. Ghanbaja, Y. Battie, A. En Naciri, F. Soldera, F. Mücklich, and D. Horwat, Local structure-driven localized surface plasmon absorption and enhanced photoluminescence in $ZnO-Au$ thin films, *J. Phys. Chem. C* **120**, 29405-29413 (2016).
- L. Broch, L. Johann, N. Stein, A. Zimmer, and R. Beck, Real time in-situ ellipsometric and gravitometric monitoring for electrochemistry experiments, *Rev. Sci. Instrum.* **78**, 064101 (2007).
- S. Liu, W. Du, X. Chen, H. Jiang, and C. Zhang, Mueller matrix imaging ellipsometry for nanostructure metrology, *Opt. Express* **23**, 17316-17329 (2015).