# Polarimetric approach for well-defined impurities detection in isotropic materials

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In this paper, a new kind of approach to reveal the presence of well-defined impurities in isotropic materials is proposed and verified against actual measurements over real samples. The rationale lies in the different polarimetric symmetry properties of inhomogeneous and isotropic materials within well-defined impurities from homogeneous ones. The underpinning physical idea is to inspect the Mueller matrix of the material sample, obtained from an ellipsometric measure: its form, in terms of symmetry, can reveal whether or not if in there are well-defined impurities in the sample.
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## 1 INTRODUCTION

Media characterization has a paramount importance in a broad range of applications including for instance buildings, chemical and mechanical industries and electronic components production. The characterization techniques depend obviously on the specific materials properties we are interested in, i.e. physical, chemical, mechanical or optical. In particular, in the field of optical characterization the most important and common approach is the spectroscopic one, whereby it is possible to analyze several properties of materials that absorb or reflect electromagnetic radiations in a wide spectral range, from NIR to UV bands. Ellipsometry is the main spectroscopic technique for media optical characterization, and its theoretical fundamentals are in depth described in several books [1]–[4]. It is based on the measurement of the polarization properties of the light beam reflected off the material surface. In this way several media features of interest, such as surface thickness, refractive index, absorption coefficient and anisotropy, can be analyzed.

Classical ellipsometric technique for media optical characterization is used to analyze properties of a broad range of materials, such as amorphous semiconductors [5], different types of thin films [6, 7], and flexible substrates [8]. This technique represents a non-destructive, reproducible, quick and accurate analysis: in fact in few minutes it is possible to analyze sample under test features of interest with a high degree of precision, for example an Å order of magnitude for thickness, without modifying its properties repeating the measure in the same conditions of previous measures. Unfortunately, this approach take in account only specular reflections, and it is able to analyze only material samples with thin surface, from nms to µms, and it is strongly dependent from surface features like roughness, polish, and so on. Furthermore, ellipsometric accuracy has to be validate from other techniques and instrumentations, like profilometer for thickness measurements, or atomic force microscopy (AFM) and Rutherford backscattering (RBS) for optical properties. In this paper we investigate an innovative use of the ellipsometric technique that exploits the Mueller polarimetric model [9]–[12].

## 2 METHODOLOGY

The proposed approach is meant at identifying a polarimetric feature peculiar to well-defined impurities within inhomogeneous and isotropic materials. The underpinning idea is to exploit symmetry properties that are proper of the Maxwell equations and that are owned by materials. These symmetries are independent of the specific scattering mechanism or, in other words, they represent an invariant property of the material under test[13]–[15]. In fact, in [13, 14] it is demonstrated that applying Lie algebra as formal structure for studying the nature of the Maxwell electromagnetic fields, the polarimetric representation via the Mueller matrix can be exploited to investigate the scattering structures in media. In well-defined impurities materials the Mueller matrix does not show reflection symmetry in the polarimetric space [13, 14], and therefore this makes the Mueller matrix off-diagonal terms not equal to zero [16]. Note that such terms can be nulled by proper change

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of the polarization basis if, and only if, the material is characterized by reflection symmetry [16].

Symmetry is a very powerful concept that applies in a wide range of scientific areas such as quantum mechanics and crystallography. Such symmetries can be easily seen through appropriate polarimetric representations [17]–[20]. On this purpose it is useful to remind the key ones.

Polarimetric reflection can be regarded as a transformation of the incident light beam into the reflected one and can be described, for nondepolarizing samples, by the Jones formalism [18]–[20]:

$$\mathbf{E}^r = \frac{e^{-jkd}}{d}\mathbf{S}\mathbf{E}^i, \tag{1}$$

where $j$ is the imaginary unit, $d$ is the distance between the sample under test and the light source (detector), $k$ is the electromagnetic wave number, $\mathbf{E}^{r(i)}$ is the bi-dimensional complex vector of the electric field of the reflected (incident) light beam decomposed in a parallel component, $E_p$, and another orthogonal one, $E_s$, with respect to the plane of incidence. For this reason, the scattering matrix $\mathbf{S}$ can be written as:

$$\mathbf{S} = \begin{pmatrix} \dot{S}_{ss} & \dot{S}_{sp} \\ \dot{S}_{ps} & \dot{S}_{pp} \end{pmatrix}, \tag{2}$$

in which each element is a complex one, with its amplitude and its phase. This kind of polarimetric model does not take in account random phenomena like scattering and depolarization, where with the term depolarization it means a coupling of energy from deterministic into stochastic modes of the field that can not be removed in no case [20]. A powerful and more general formalism which is able to account for depolarizing processes is based on the Stokes parameters [18]–[20]:

$$\mathbf{s}^s = \frac{1}{(kd)^2}\mathbf{M}\mathbf{s}^i, \tag{3}$$

where $\mathbf{s}$ is the Stokes vector related to measurable quantities like light intensity, $\mathbf{M}$ is the 4 x 4 Mueller matrix of the sample and the ratio is a normalization factor, very often omitted in literature, that make its elements dimensionless and independent of the distance $d$ [19]. This is a second order incoherent scattering model which, due to its capability to account for both fully (i.e. nondepolarizing phenomena like the Faraday rotation) and partially polarized light waves, is the most elegant and general way to deal with polarimetric scattering [19, 21, 22]. Each element of the Mueller matrix is an ensemble average of combinations of the scattering amplitudes, and in the most general case they are all 16 independent parameters. However, both symmetry properties and scattering geometry can simplify the Mueller matrix structure reducing the number of independent parameters, as when reciprocity is applied. In this study, reflection symmetry is accounted for since all homogeneous and isotropic materials satisfy this property. A scattering sample, that satisfies reflection symmetry, is such that for each elementary scattering area, with its own scattering matrix $\mathbf{S}_{\Delta\prime}$, there is always a matching one, which is reflection symmetric with respect to the plane of incidence, and it is characterized by a scattering matrix $\mathbf{S}_{\Delta\prime\prime}$, whose off-diagonal elements have a reversed sign:

$$\mathbf{S} = \begin{pmatrix} \dot{S}_{ss} & -\dot{S}_{sp} \\ -\dot{S}_{ps} & \dot{S}_{pp} \end{pmatrix}. \tag{4}$$

Hence, if at $\mathbf{S}_{\Delta\prime}$ corresponds $\mathbf{M}_{\Delta\prime}$, then at $\mathbf{S}_{\Delta\prime\prime}$ corresponds a $\mathbf{M}_{\Delta\prime\prime}$ such that the resulting $\mathbf{M}_{rs}$ in case of reflection symmetry is [23]:

$$\mathbf{M}_{rs} = \mathbf{M}_{\Delta\prime} + \mathbf{M}_{\Delta\prime\prime} = \begin{pmatrix} M_{11} & M_{12} & 0 & 0 \\ M_{21} & M_{22} & 0 & 0 \\ 0 & 0 & M_{33} & M_{34} \\ 0 & 0 & M_{43} & M_{44} \end{pmatrix}. \tag{5}$$

The Eq. (5) shows that reflection symmetry manifests itself in the polarimetric scattering by nulling off-diagonal blocks, that are representative of the correlation between like- and cross-polarized scattering amplitudes [13, 17]:

$$\langle \dot{S}_{ss}\dot{S}^*_{sp}\rangle = \langle \dot{S}_{sp}\dot{S}^*_{pp}\rangle = 0, \tag{6}$$

where $\langle\cdot\rangle$ and $*$ stand for mean ensemble average and complex conjugate, respectively. Hence, $\mathbf{M}_{rs}$ consists of only eight nonzero elements and five independent parameters. The Mueller matrix form shown in Eq. (5) is typical of homogeneous and isotropic materials, but also of anisotropic materials[8, 26, 27]. So, analyzing the Mueller matrix, whose structure depends on the symmetry properties of the observed material sample, it is possible to find out well-defined impurities only in isotropic samples. The presence of well-defined impurities in a material sample breaks the reflection symmetry, so its Mueller matrix form is not the same of Eq. (5): in fact, this kind of impurities results in strong departure from reflection symmetry. To quantify the degree of inhomogeneity we propose an index, the Mueller matrix ratio, to measure the departure from reflection symmetry:

$$MMR = 10\log_{10}\left|\frac{M_{ond}}{M_{offd}}\right|, \tag{7}$$

where $M_{ond}$ and $M_{offd}$ are any chosen elements from on-diagonal matrix blocks and from off-diagonal matrix blocks, respectively. A high value of the MMR is representative of an homogeneous and isotropic material sample, whose Mueller matrix follows the form in Eq. (5). A low value of the MMR stands for the presence of well-defined impurities in the material sample observed, that break reflection symmetry in the Mueller matrix form.

## 3 EXPERIMENTS

To verify the proposed polarimetric approach to well-defined impurities detection we conduct several tests with an ellipsometric working station composed of a spectroscopic phase modulation ellipsometer UVISEL device and its own management software DeltaPsi2. Main features of the UVISEL device are the photoelastic modulator at 50 kHz, the light source/detector system formed by a Xenon arc lamp of 75 W and a photodiode array, and a spot size of 1200 μm. The working station manufacturer states that the error on the Mueller matrix elements measurement varies in the range $10^{-2}$ - $10^{-3}$. Furthermore, since the matrix is measured in an indirect way inasmuch it is obtained from ellipsometric angles, it is right to report that ellipsometric angles are measured, in a straight-through air configuration 1.5 - 5 eV, with an accuracy of $\Psi^\circ = 45^\circ \pm 0.02^\circ$ and $\Delta^\circ = 0^\circ \pm 0.02^\circ$ [28]. The device can measure the normalized Mueller matrix of the analyzed sample, but due to hardware and software issues it is unable to

measure the fourth row of the matrix. Nevertheless, the effectiveness of this kind of approach was confirmed by this incomplete experimental setup. As a consequence, these experimental measurements are only a necessary test of the theory described in section II.Measurements are made in a wide range of wavelength from NIR to UV bands, obtaining an average matrix. Furthermore, to perform the ellipsometric measure each test was made choosing an angle of incidence (AOI) closer to the Brewster angle of the material under test. First experiment was made on a pure gold substrate, whose features are reported in the Table 1. The normalized Mueller matrix obtained is:

$$\mathbf{M} = \begin{pmatrix} 1 & -0.106 & -0.011 & -0.005 \\ -0.014 & 0.999 & 0.005 & 0.001 \\ 0.025 & -0.001 & -0.750 & -0.518 \\ - & - & - & - \end{pmatrix}. \quad (8)$$

The experimental procedure for the evaluation of the MMR is based on the random selection of a pair of Mueller matrix elements, one from the on-diagonal blocks and the other from the off-diagonal ones. Choosen this pair, the MMR has been evaluated in according to Eq. (7). These steps have been repeated for a thousand times from the same acquired matrix, and all the MMR values shown in this paper are averaged results. The mean value of the MMR calculated for this first type of material sample is 19.184 dB: this means that on-diagonal block elements are about a hundred times bigger than off-diagonal block ones. A second test, made on an inhomogeneous gold sample contaminated by chrome impurities due to manufacturing process (see Table 2), confirms that such a sample, in despite of the presence of impurities, shows the same Mueller matrix form of the Eq. (5). From this point of view, this kind of inhomogeneous samples has to be considered homogeneous, in terms of absence of well-defined impurities.

| SUBSTRATE | *Pure Gold*<br>*Thickness 700 μm* |
|---|---|
| SURFACE | *Thickness 15nm*<br>*Roughness 21%* |
| AOI | 60° |
| RANGE | *300 - 1600 nm* |

TABLE 1 Case I: Homogeneous and isotropic material

| SUBSTRATE | *Pure Silicon*<br>*Thickness 500 μm* |
|---|---|
| SURFACE | *Gold 66% — Chrome 34%*<br>*Thickness 11 nm* |
| AOI | 65° |
| RANGE | *310 - 800 nm* |

TABLE 2 Case II: Inhomogeneous and isotropic material with random impurities

The matrix acquired is the following:

$$\mathbf{M} = \begin{pmatrix} 1 & -0.711 & -0.016 & -0.003 \\ -0.720 & 1.009 & -0.004 & -0.002 \\ 0.032 & -0.016 & -0.619 & -0.237 \\ - & - & - & - \end{pmatrix}, \quad (9)$$

that leads to a MMR of 19.407 dB, of the same order of magnitude of a homogeneous material. The rationale is to be searched in the totally random distribution of the chrome impurities, which holds reflection symmetry and preserves the symmetric Mueller matrix form. This measure was made in a restricted spectral range due to the too low signal level in the NIR band. To show the effectiveness of the proposed approach it was analyzed, for the third experiment, a ThorLabs test target designed to quantitatively test optical system performance in terms of resolution and to provide length calibration for microscopy. These targets consist of groups of line space patterns, whose spatial frequency varies: this deterministic structure printed on the substrate represent a well-defined impurity for the whole material sample. Main features of the ThorLabs test target are reported in Table 3. The Mueller matrix measured for a line pattern with 0.397 cycles for mm and a line thickness of 1.259 mm is:

$$\mathbf{M} = \begin{pmatrix} 1 & -0.478 & 0.464 & -0.012 \\ -0.406 & 0.558 & -0.299 & -0.392 \\ 0.490 & -0.405 & 0.644 & -0.340 \\ - & - & - & - \end{pmatrix}, \quad (10)$$

and the evaluated MMR is 3.781 dB, very lower with respect to the previous ones and representative of a situation in which all matrix elements are about of the same magnitude. In this case, in fact, the printed chrome microstrips act for well-defined impurities that break reflection symmetry. These results are independent of the sample orientation in the azimuthal plane and in the plane of incidence, due to the theoretical background described in section II.Furthermore, other experiments, made on sample surface areas with different impurities spatial frequency, show the same type of results. Obviously, this is true only when the chrome microstrips spatial frequency is such that the spot illuminates both substrate and impurities.

| LABEL | *ThorLabs USAF 1951*<br>*Standard MIL-S-150A* |
|---|---|
| SUBSTRATE | *Pure Glass*<br>*Thickness 1.5 mm* |
| SURFACE | *Chrome Microstrips*<br>*Thickness 120 nm* |
| AOI | 65° |
| RANGE | *300 - 800 nm* |

TABLE 3 Case III: Inhomogeneous and isotropic material with well-defined impurities

Note that although the AOI choice is not generally significant, this case requires an appropriate choice to allow the detection of the well-defined impurities. In fact, to be able to observe the impurities, it requires a right AOI value, approximately intermediate between substrate and impurities Brewster angle. Although the proposed approach is unable to distinguish, when material samples without well-defined impurities are analyzed, isotropic materials from anisotropic ones, it is possible to merge this experimental procedure with a classical ellipsometric measure (with the same working station) to obtain the desiderable information about this kind of features.

## 4 CONCLUSION

In this paper we proposed a polarimetric approach to find out well-defined impurities in isotropic material samples. This ap-

proach is based on an electromagnetic model to exploit the different symmetry properties that characterize well-defined impurities within inhomogeneous materials, and homogeneous materials. On this physical basis, an index to quantify the difference between the two kind of materials in terms of reflection symmetry property is proposed. The goodness and effectiveness of this technique is verified against first experiments made with an ellipsometric instrumentation over real samples.

## References


[1] H. Fujiwara, *Spectroscopic Ellipsometry Principles and Applications* (Wiley, Tokyo, 2007).

[2] M. Born, and E. Wolf, *Principles of Optics* (Pergamon Press, Bath, 1970).

[3] G. E. Jellison Jr., "Spectroscopic ellipsometry data analysis - Measured versus calculated quantities," Thin Solid Films **313**, 33–39 (1998).

[4] G. E. Jellison Jr., "Data analysis for spectroscopic ellipsometry," Thin Solid Films **234**(1-2), 416–422 (1993).

[5] G. E. Jellison Jr., V. I. Merkulov, A. A. Puretzky, D. B. Geohegan, G. Eres, D. H. Lowndes, and J. B. Caughman, "Characterization of thin film amorphous semicondutcors using spectroscopic ellipsometry," Thin Solid Film **377**, 68–73 (2000).

[6] G. E. Jellison Jr., L. A. Boatner, D. H. Lowndes, R. A. McKee, and M. Godbole, "Optical functions and transparent thin films of SRTI03, BATI03, and SIOX determined by spectroscopic ellipsometry," Appl. Optics **33**, 6053–6058 (1994).

[7] O. Pena-Rodriguez, C. F. Sanchez-Valdes, M. Garriga, M. I. Alonso, X. Obradors, and T. Puig, "Optical properties of ceria-zirconia epitaxial films grown on chemical solutions)," Mater. Chem. Phys **138**, 462–467 (2013).

[8] M. Stchakovsky, C. Caillaud, M. Foldyna, R. Ossikovski, and E. Garcia-Caurel, "Polarimetric characterization of optically anisotropic flexible substrates," Thin Solid Films **516**, 1414–1418 (2008).

[9] R. M. A. Azzam, "Ellipsometry," in *Handbook of Optics*, M. Bass, eds., Ch. 16 (Third edition, McGraw-Hills, New York, 2009).

[10] R. M. A. Azzam, "Mueller matrix ellipsometry: a review," P. Soc. Photo-Opt. Ins. **396** 400–409 (1997).

[11] G. E. Jellison Jr., *Ellipsometry data analysis: a tutorial* (Oak Ridge National Laboratory, University of Michigan, 2000).

[12] D. Schmidt, *Generalized ellipsometry on sculptured thin films made by glancing angle deposition* (Ph.D. dissertation, University of Nebraska, 2010).

[13] C. E. Baum, and H. N. Kritikos (eds.), *Electromagnetic Symmetry* (Taylor and Francis, New York, 1995)

[14] S. V. Nghiem, S. H. Yueh, R. Kwok, and F. K. Li, "Symmetry properties in polarimetric remote sensing," Radio Sci. **27**, 693–711 (1992).

[15] W. C. Chew, "A new look at reciprocity and energy conservation theorems in electromagnetics," IEEE T. Antenn. Propag. **56**, 970–975 (2009).

[16] F. Nunziata, M. Migliaccio, and C. E. Brown, "Reflection symmetry for polarimetric observation of man-made metallic targets at sea," IEEE J. Oceanic Eng. **37**, 384–394 (2012).

[17] S. H. Yueh, R. Kwok, and S. V. Nghiem, "Polarimetric scattering and emission properties of targets with reflection symmetry," Radio Sci. **29**, 1409–1420 (1994).

[18] J. J. Gil, "Polarimetric characterization of light and media," Eur. Phys. J-Appl. Phys. **40**, 1–47 (2007).

[19] A. Guissard, *Introduction to radar polarimetry* (Technical report of the Laboratoire de Télécommunications et Télédetection of the Faculté des Sciences Appliquées Université catholique de Louvain, 2000).

[20] S. R. Cloude, *Polarisation: Applications in Remote Sensing* (Oxford Press, New York, 2009).

[21] J. J. van Zyl, C. H. Papas, and C. Elachi, "On the optimum polarization of incoherently reflected waves," IEEE T. Antenn. Propag **35**, 818–826 (1987).

[22] J. J. Gil, and E. Bernabeu, "A depolarization criterion in Mueller matrices," Opt. Acta **32**, 259–261 (1985).

[23] A. Schonhofer, and H. G. Kuball, "Symmetry properties of the Mueller matrix," Chem. Phys. **115**, 159–167 (1987).

[24] C. E. Baum, "Symmetry in electromagnetic scattering as a target discriminant," P. Soc. Photo-Opt. Ins. **3120**, 295 (1997).

[25] C. E. Baum, "Symmetry in target recognition," in *Proceedings to the Fourth International Conference on Ultrawideband Ultrashort Impulse Signals*, 12–15 (Sevastopol, Ukraine, 2008).

[26] D. M. Rosu, *Ellipsometric characterization of anisotropic thin organic films* (Ph.D. dissertation, Technischen Universitat Berlin, 2010).

[27] A. C. Galca, *Ellipsometric studies of anisotropic nanoscaled media* (Ph.D. dissertation, University of Twente, 1977).

[28] J. Yvon, *Spectroscopic Ellipsometry User Guide* (HORIBA, Irvine, 2008).