Journal of Alloys and Compounds 504S (2010) S405–S409

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Environmental monitoring by thin film nanocomposite sensors for cultural heritage preservation

Baoying Liu [a], Xiaojiang Chen [b], Dingyi Fang [b], Alessio Perrone [c,*], Stergios Pispas [d], Nikos A. Vainos [d,e]

[a] Advanced School-ISUFI, Cultural Heritage Department, University of Salento, 73100 Lecce, Italy
[b] School of Information Science and Technology, Northwest University, 710069 Xi'an, China
[c] University of Salento, Physics Department and INFN, Via Arnesano, 73100 Lecce, Italy
[d] National Hellenic Research Foundation, TPCI, 48, Vas. Constantinou Ave., 16135 Athens, Greece
[e] University of Patras, Department of Materials Science, 26504 Patras, Greece

ARTICLE INFO

Article history:
Received 12 July 2009
Received in revised form 11 February 2010
Accepted 21 February 2010
Available online 3 March 2010

Keywords:
Art conservation
Sensors
Thin films
Laser processing
Nanocomposites
Photonics

ABSTRACT

Environmental control is a crucial issue in cultural heritage preservation as it especially relates to sensitive artwork and antique object conservation. Storage and transport of artworks and antiques are operations requiring precise control of the environment. Current technology trends lead to miniaturization of environmental sensor devices in which low power dissipation and advanced non-contact or remote monitoring methods appear to offer significant advantages.

In the above context, nanocomposite materials represent innovative alternative solutions for high sensitivity temperature and relative humidity (RH) sensing. The control of both of these parameters, together with the exposure to ultraviolet radiation, is important in minimizing aging and deterioration of art and antique objects. New schemes reported here consider the classes of CN_x and $CoCl_2$ nanocomposites. First, CN_x thin films are synthesized on Si substrates by reactive pulsed laser ablation of graphite targets in N_2 atmosphere to form capacitive sensors. On the other hand, $CoCl_2$ polymer matrix composite films are produced by spin coating or casting of the composite polymer/$CoCl_2$ on planar glass substrates. These latter systems present a new class of optically interrogated photonic sensors featuring powerless sensing head and remote monitoring capabilities. The prototype devices proposed for use in art conservation and museum applications have been tested under controlled environmental conditions and their performance is seen to be comparable, and in some cases superior, to conventional monitoring solutions.

1. Introduction

The preservation of cultural heritage attracts universal attention and new regulations focus on the application of new technologies in conservation, exhibition, storage and transport. To minimize the effects of aging, renovation or logistics operations, monitoring and controlling of the indoor ambient, or even better, the micro-climate of the cultural object is crucial. Such aspect is well recognized in museums, storage facilities, libraries, archives, galleries for ensuring the long-term preservation, safety and preventive conservation of artworks, antiques and archaeological collections. Among the most important environment factors affecting the precious items are the temperature, the relative humidity and the chemical environment. Furthermore, mechanical vibration and ultraviolet light exposure enhance and accelerate the damaging effects. Fluctuations in RH and temperature can cause several kinds of damage and deterioration such as dimensional change, chemical reactivity and bio-deterioration of museum objects, which are often made of non-isotropic materials [1–3]. Continuous environmental monitoring and the assurance of stable conditions in the local environment of the precious artwork constitute an imperative need in order to preserve the precious items for long periods of time. A main goal of preventive conservation is to maintain the artworks and collections under basically constant levels of temperature and RH and thus a precise control of these physical parameters is a strict requirement.

In this context, increasing recent interest in the field of cultural heritage points to a new generation of sensors tailored for applications in indoor environment of museums [4,5]. Sensors for such application must display a number of characteristics, such as high sensitivity, non-contact operation, stability and robustness, relatively fast temporal response and recovery time, while maintaining a miniature size, low cost and a low power operational character, which is associated with the reduced power (thermal) dissipation in the area.

* Corresponding author. Tel.: +39 0832 297501; fax: +39 0832 297501.
E-mail address: alessio.perrone@le.infn.it (A. Perrone).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.02.147

In reference to the relative humidity monitoring, a range of conventional devices already exist and involve infrared hygrometers, aspiratory psychrometers and capacitive or resistive type sensors. Such commercially available technology is relatively bulky and requires complex electronics to be placed close to the precious object, while the interrogation is purely electrical, which is vulnerable to electromagnetic interference effects.

Currently advanced fabrication methods lead to new classes of materials characterized by their nanocomposite material structure which offer advanced functionalities. Among this new generation of sensors, a class of nitride based CN_x/Si films and a second class of hybrid polymer/cobalt chloride composite structures show increased potential performance for temperature and RH sensing [6–8]. In optics a variety of materials may be synthesized, investigated and used as humidity sensors by monitoring changes of optical transmission [9,10]. This paper proposes the use of such advanced technology in the field of cultural heritage and focuses on the design, fabrication, characterization and testing of these classes of sensors.

2. Experimental

2.1. Carbon nitride sensors grown by reactive pulsed laser deposition

CN_x/Si thin heterostructures were prepared by multipulse laser ablation of graphite targets in low-pressure (5 Pa) nitrogen ambient. The flux of high purity nitrogen (electronic grade 99.999%) was continuously blown inside the deposition system. Fig. 1 shows the apparatus used for reactive pulsed laser deposition (RPLD) experiments. It consists mainly of a stainless-steel vacuum system, pumped to a base pressure of 10^{-5} Pa by a turbomolecular pump, and an UV XeCl excimer laser working at 308 nm (Lambda-Physik, LPX 315i). The laser beam was focused on nuclear-grade graphite targets with a MgF_2 lens having 30 cm focal length. It fell on the target surface with an incident angle of about 45°. Target was rotated with a frequency of 3 Hz to avoid drilling. Si substrate was placed in front and parallel to the target at distance of 4 cm. Films were deposited with 10^4 subsequent pulses at 10 Hz repetition rate with laser fluence of 12 J/cm^2. The present experimental conditions were chosen after systematic parametric studies. Before each deposition, the vacuum system was backed to improve the quality of the vacuum.

Several samples were prepared to optimize the deposition process. However, only few specimens were sampled out for testing. All deposited films were characterized by an array of diagnostic techniques, here omitted for the sake of brevity.

2.2. Nanocomposite photonic sensors

Photonic sensors are considered to be suitable for humidity sensing since they have small size and weight, they show immunity to electromagnetic interference, non-corrosiveness, remote sensing and the potential for multiplexing the information from a large number of sensors using a single fiber.

The sensor proposed in the present work is a hybrid organic–inorganic material consisting of polyethylene oxide (PEO) and cobalt chloride ($CoCl_2$) and it is based on absorption changes of the inorganic salt. So far cobalt chloride has been used as a colorimetric indicator of humidity because of its color changes upon complexation with water molecules [11]. Anhydrous $CoCl_2$ is a deep blue inorganic salt which exhibits strong absorption bands in the range of 550–710 nm, while the fully hydrated material $CoCl_2{\cdot}6H_2O$ is a pink colored material which absorbs weakly at the range of 410–550 nm.

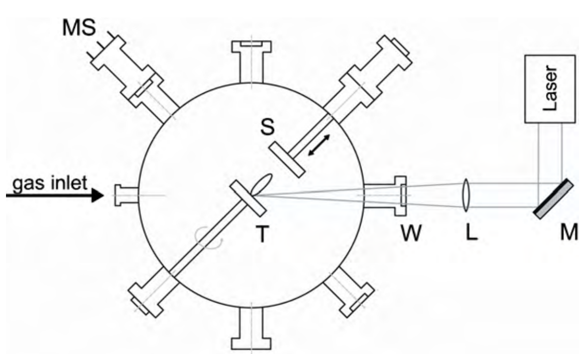

Fig. 1. RPLD experimental set-up. MS: mass spectrometer; L: lens; T: target; S: substrate; W: laser window; M: mirror.

Humidity detection is achieved by monitoring the alterations of optical diffraction effects attributed to the surface modification in the polymer/$CoCl_2$ composites. We note here that in the thin film case the absorption effects are practically absent. This aspect corroborates the remote sensing potential of the device, in which the minimization of light loss is needed.

PEO has been synthesized by anionic polymerization. Purification of all reagents used, such as solvents, monomers was achieved by well-established procedures. The homopolymers were prepared with the addition of n-butyllithium as initiator and phosphazine base as a polymerization promoter. The polymerization was terminated by the addition of methanol to give the solid polymer. The resulted material has a molecular weight of 50 K and a polydispersity of 1.05 (M_w/M_n). Its glass transition T_g is −40 °C and its melting point is ~55 °C as indicated by Differential Scanning Calorimetry (i.e., the polymer is semicrystalline at room temperature). The molecular weight and molecular weight distribution data were obtained by size exclusion chromatography using a Waters system composed of Waters 1515 isocratic pump, a set of three μ-Styragel mixed bed columns, with a porosity range of 10^2 to 10^6 Å, a Waters 2414 refractive index detector and operating through Breeze software. Tetrahydrofurane containing 5% triethylamine was the mobile phase used at a flow rate of 1.0 mL/min at 40 °C. Calibration was performed using narrow dispersion polystyrene standard. The polymer was co-dissolved with the desired amount of $CoCl_2$ in water with PEO polymer concentration constant and varying the concentration of $CoCl_2$ between 5 and 10 wt% with respect to the polymer mass.

The final solution was spin-coated or cast on glass substrates and in some cases on prefabricated grating structures. The film thickness varied between 100 and 300 nm for the case of the composite material on plain glass substrates, and 10–30 μm for the case of the grating structures. The measurements of thickness and surface roughness were performed by using a KLA Tencor, Alpha-Step 500 IQ, surface profiler.

3. Results and discussion

It is well known that CN_x/Si thin heterostructures are considered to be promising candidates as humidity sensors [6]. In the present paper capacitance changes with the temperature have also been observed. The capacitance–voltage characteristics of the CN_x/Si thin heterostructures at 77 and 300 K and at 1 MHz are shown in Fig. 2. The voltage was applied to Al contact dots grown on the CN_x surface. The curves reported in Fig. 2 show that the CN_x/Si heterostructure is a metal-insulator-semiconductor type. The highest capacitance reached at 77 K is 110 nF cm^{-2}, while at 300 K the maximum value is about 70 nF cm^{-2}. This high sensitivity of the capacitance over the temperature, suggests that the present structure can be used as very sensitive temperature sensor. The application of these films as stable and robust sensors in indoor environments will be the subject of our future investigations.

A new alternative approach is described in the experimental photonic RH sensing in planar layered or grating composites. In this case a sensor head consisting of a nanocomposite thin solid film is exposed to the environment. The optical properties of the film,

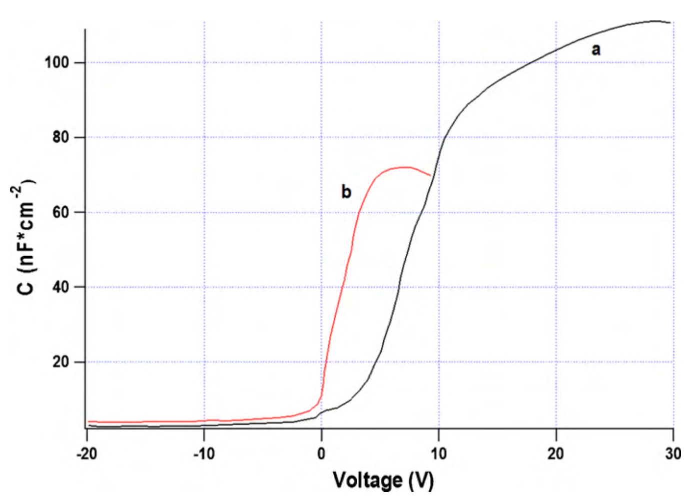

Fig. 2. Capacitance vs applied voltage of thin CN_x/Si heterostructures at 1 MHz at (a) 77 K and (b) 300 K.

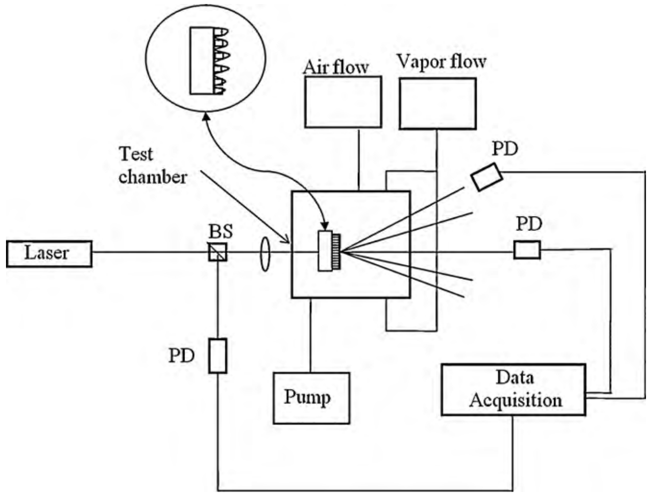

Fig. 3. Experimental station for environmental photonic sensing. The sensor interrogation is performed by laser beams transmitted and diffracted from the structure (BS: beam splitter; PD: photodiode). In the inset is shown the schematic outline of the composite grating structure used for enhancing performance.

especially the diffractive properties, are altered and such effects are monitored by a laser beam transmitted from a remote point through the structure.

The experimental station comprises an optically transparent test chamber connected with dry air and vapor mixtures via teflon pipes (Fig. 3). The dry and humid air was produced by a water bubble humidifier. The vapor flow was controlled by premixing, while humidity monitoring inside the test chamber was performed by using a commercial humidity probe. The samples were inserted in the chamber and investigated in alternating humidity variation cycles ranging from 20% to 80% RH. A He–Ne laser emitting at 633 nm was used as the optical source. Transmitted intensity signal for various diffraction orders was measured by a double channel power meter (Newport Model 2832-C). A reference signal was also recorded to account for possible instabilities of the optical power during tests. A spatial filter was also used for the optimization of transmitted or diffracted signal for various orders. Measurements were recorded and simultaneously displayed on a PC using a data acquisition system connected on the optical power meter output via the RS232 port.

In order to understand the sample's response mechanism to RH, its surface was studied using a microscope set-up in which color filters could be used in order to test for absorption effects. In partic-

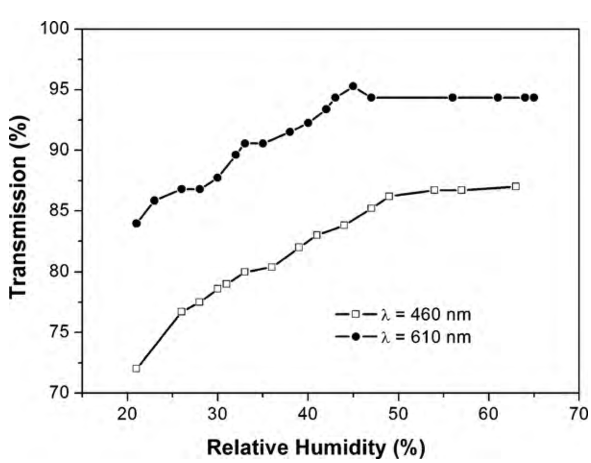

Fig. 4. Response of PEO/$CoCl_2$ hybrid at different levels of humidity for two wavelengths (after [10]).

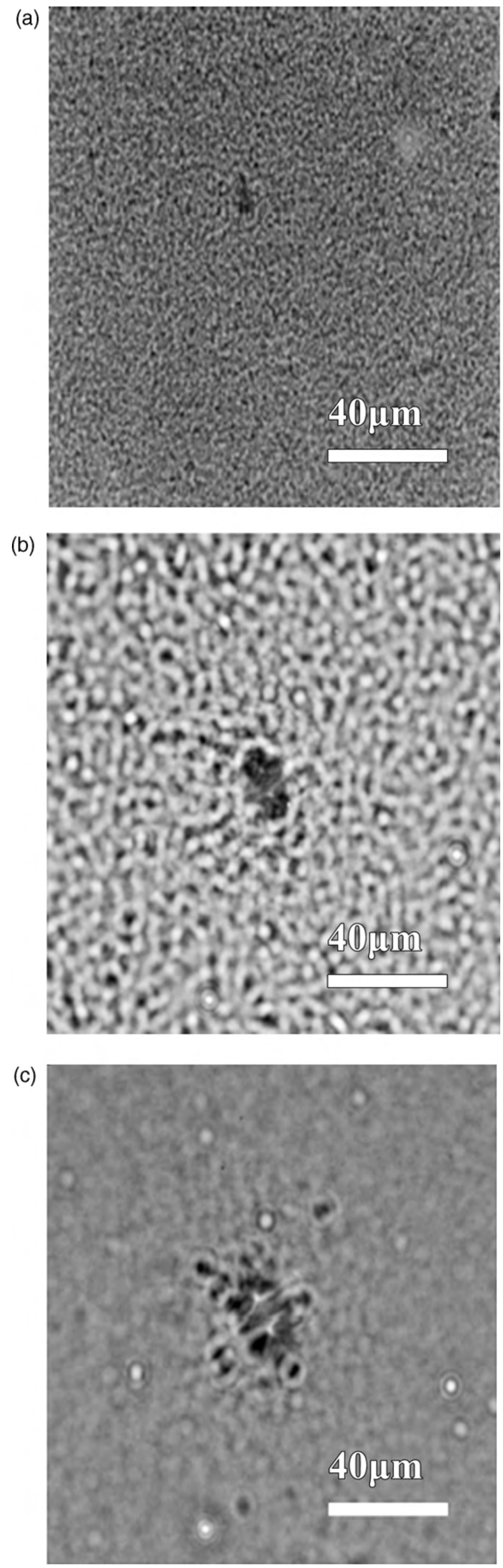

Fig. 5. Optical micrographs of the surface of the PEO/$CoCl_2$ hybrid film at different levels of humidity: (a) RH = 21%; (b) RH = 45% and (c) RH = 70% (length of scale marker is 40 μm) (after [10]).

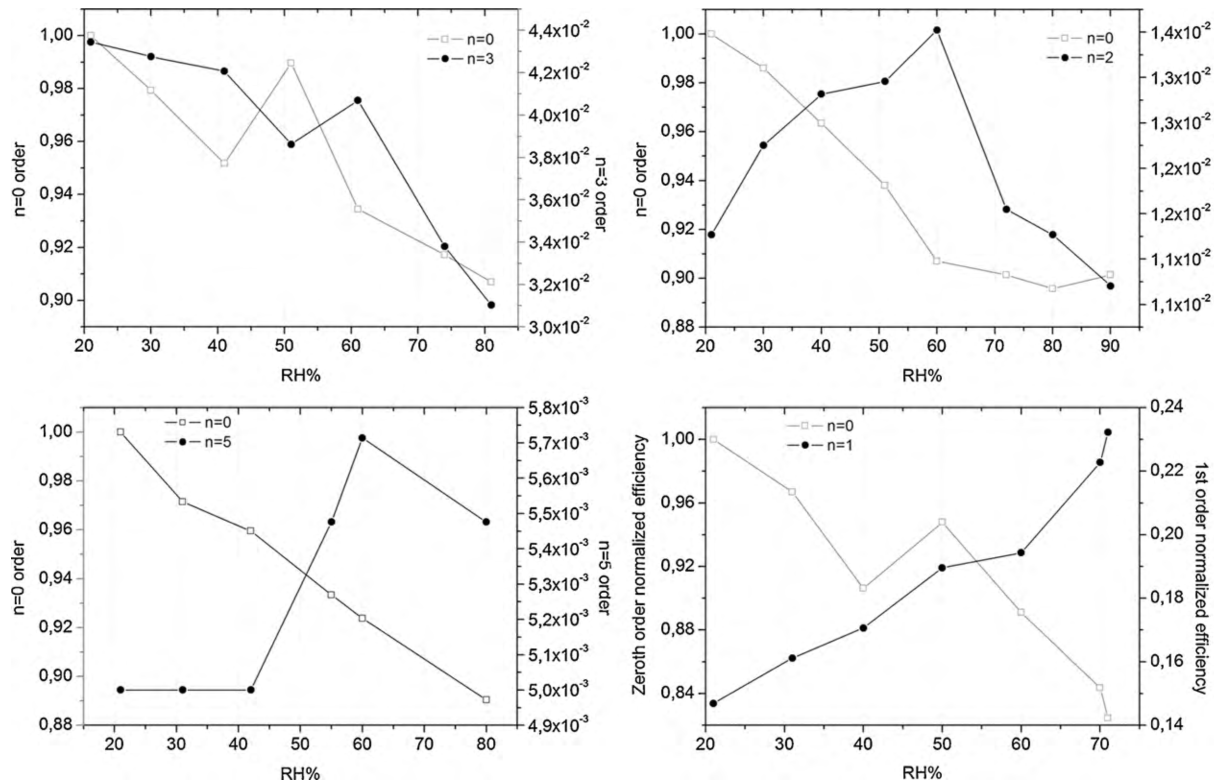

Fig. 6. Normalized diffraction efficiency for various orders for a PEO/$CoCl_2$ hybrid system in respect to RH%.

ular, a sample was illuminated by white light at different RH levels. In the case of the dry sample (21% RH), the surface does not have any cracks, however it has granulated features due to the formation of localized nano- and microcrystals. On increasing humidity, i.e. RH 45%, the granulated features begin to disappear, while for RH 71% they vanish completely. Cycling tests have been performed which proved that the effect is fully repeatable and no residual changes have been observed. Surface morphology variations were monitored in the range of 150 nm. The effect is attributed to the formation of localized $CoCl_2$ clusters in the matrix, which incorporates water molecules and form $CoCl_2{\cdot}xH_2O$ complex, changing strongly the surface morphology but with a reversible mechanism.

The optical response of the hybrid PEO/$CoCl_2$ material was also monitored for various humidity levels at two different wavelengths and is presented in Fig. 4. There is observed an increase in the transmitted optical power at lower RH values which increases and reaches saturation at RH ~50–55%.

Further on, the hybrid PEO/$CoCl_2$ material was spin-coated or casted on grating structures. The film thickness was in the range of 100–300 nm. In Fig. 5, optical microscope images of PEO/$CoCl_2$ cast on a 100 μm period prefabricated grating at different levels of humidity are shown.

A sketch outline of the composite grating structure is depicted in the inset of Fig. 3.

The redistribution of optical energy in the PEO/$CoCl_2$ system observed among various diffraction orders upon RH modification is depicted in Fig. 6. The simultaneous monitored signal values for the undiffracted beam and the diffracted order is presented. The zero order is moving towards lower intensities at higher RH, while the higher diffraction order's intensity values are increasing for RH up to 60%. The hybrid's response due to the alteration of the optical grating morphology in combination with a refractive index modification leads in changes of the diffraction efficiency. The optical response in certain orders is dependent on the salt concentration as well as on the geometrical characteristics of the grating structures. Over a certain RH value, a decrease of the diffracted beam intensity is observed. This effect is repeatable and is affected by the geometrical and refractive characteristics of the grating, characteristics which determine the diffraction efficiency variation.

The use of fiber optics and specially produced gratings represent alternative solutions for remote environments. The sensor may be embodied on a fiber optic thus forming an integrated sensing and transmission device, while further work is in progress to incorporate multiplex sensing heads for sensing a variety of chemical agents.

4. Conclusions

Art and antique conservation, transport and storage operations, require severe climatic control. Environmental sensors based on advanced fabrication technologies are proposed here for application in the sensitive field of cultural heritage preservation. These schemes comprising an increased miniaturization potential, which together with the enhanced performance and the flexible remote interrogation potential offer alternative low cost solutions in the field.

According to the proposed technologies, carbon nitride films deposited by RPLD are very promising candidates for miniature capacitance temperature sensors. The application of these devices as stable and robust sensors in indoor environments will be the subject of our future investigations. In addition an alternative photonics technology involves nanocomposite structures which alter their optical properties upon exposure to the environment. In this present first approach cobalt chloride composites are presented here for RH monitoring. The remarkable feature to interrogate the RH sensor by a laser beam transmitted through a transparent exhibition offers unique application potential. Further work on the topic as especially applied to cultural preservation applications is under way.

Acknowledgements

Work on photonic sensors is supported by projects EU IST NANOPHOS and Hellenic GSRT PENED NYVRIPHOS.

References

[1] M. Bacci, C. Cucci, A.A. Mencaglia, A.G. Mignani, Sensors 8 (2008) 1984–2005.
[2] N.S. Brommelle, Stud. Conserv. 9 (1964) 140–152.
[3] A.G. Mignani, R. Falciai, C. Trono, in: S. Martellucci, A.N. Chester, A.G. Mignani (Eds.), Optical Sensors in Microstructures, Kluwer Academic, New York, 2000, pp. 253–258.
[4] M.F. Mecklenburg, C.S. Tumosa, Ashrae J. 4 (1999) 77–82.
[5] N. Carmona, M.A. Villegas, J.M. Fernandez-Navarro, Sens. Actuators A: Phys. 116 (2004) 398–404.
[6] L.M. Zambov, C. Popov, M.F. Plass, A. Bock, M. Jelinek, J. Lancok, K. Masseli, W. Kulisch, Appl. Phys. A 70 (2000) 603–606.
[7] A. Meristoudi, L. Athanasekos, M. Vasileiadis, S. Pispas, G. Mousdis, E. Karoutsos, D. Alexandropoulos, H. Du, A. Tsigara, K. Kibasi, A. Perrone, N.A. Vainos, J. Opt. A: Pure Appl. Opt. 11 (2009) 034005.
[8] F.J. Arregui, Z. Ciaurriz, M. Oneca, I.R. Matias, Sens. Actuators B: Chem. 96 (2003) 165–172.
[9] S. Tao, C.B. Winstead, J.P. Singh, R. Jindal, Opt. Lett. 27 (2002) 1382–1384.
[10] A. Tsigara, G. Mountrichas, K. Gatsouli, A. Nichelatti, S. Pispas, N. Madamopoulos, N.A. Vainos, H.L. Du, F. Roubani-Kalantzopoulou, Sens. Actuators B: Chem. 120 (2007) 481–486.
[11] B. Yang, B. Aksak, Q. Lin, M. Sitti, Sens. Actuators B: Chem. 114 (2006) 254–262.