

Bandgap widening in thermochromic Mg-doped VO2 thin films: Quantitative data based on optical absorption

Shu-Yi Li, Nuru R. Mlyuka, Daniel Primetzhofer, Anders Hallén, Göran Possnert, Gunnar A. Niklasson, and Claes G. Granqvist

Citation: Applied Physics Letters **103**, 161907 (2013); doi: 10.1063/1.4826444
View online: http://dx.doi.org/10.1063/1.4826444
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/103/16?ver=pdfcov
Published by the AIP Publishing

Advertisement:



This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.238.20.154 On: Wed, 23 Oct 2013 14:31:29

Bandgap widening in thermochromic Mg-doped VO_2 thin films: Quantitative data based on optical absorption

Shu-Yi Li,[1,a)] Nuru R. Mlyuka,[1,2] Daniel Primetzhofer,[3] Anders Hallén,[4] Göran Possnert,[3] Gunnar A. Niklasson,[1] and Claes G. Granqvist[1]
[1]*Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden*
[2]*Department of Physics, University of Dar es Salaam, P.O. Box 35063, Dar es Salaam, Tanzania*
[3]*Department of Physics and Astronomy, The Ångström Laboratory, Uppsala University, P.O. Box 516, SE-75120 Uppsala, Sweden*
[4]*KTH-ICT, Royal Institute of Technology, Electrum 229, SE-164 40 Kista-Stockholm, Sweden*

(Received 1 September 2013; accepted 7 October 2013; published online 18 October 2013)

Thermochromic Mg-doped VO_2 films were deposited by reactive direct current magnetron sputtering onto heated glass and carbon substrates. Elemental compositions were inferred from Rutherford backscattering. Optical bandgaps were obtained from spectral transmittance and reflectance measurements—from both the film side and the back side of the samples—and ensuing determination of absorption coefficients. The bandgap of Mg-doped films was found to increase by 3.9 ± 0.5 eV per unit of atom ratio $Mg/(Mg+V)$ for $0 < Mg/(Mg+V) < 0.21$. The presence of ~0.45 at. % Si enhanced the bandgap even more. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4826444]

This Letter shows that Mg-doped thermochromic VO_2 thin films display strong bandgap widening proportionate to the Mg content.

Thermochromism of VO_2 was discovered more than half a century ago.[1] This material is known to undergo a first order metal-to-insulator transition accompanied by a crystal structure transformation, and thin films of VO_2 reversibly switch between a low-temperature (monoclinic, M1) infrared-transmitting semiconducting state and a high-temperature (rutile) infrared-reflecting metallic state at a critical temperature τ_c of ~68 °C. The underlying mechanism is connected to a Mott–Hubbard transition and/or a Peierls mechanism and is of continued scientific interest;[2–7] it was recently described as a solid-state triple point.[2] The switching of the infrared transmittance enables a modulation of the solar energy throughput, which has led to large practical interest in thermochromic VO_2 as smart switchable coatings for energy-efficient windows.[8–11] The requirements for window applications is that the VO_2-based films simultaneously possess[12] (i) a low τ_c, ideally close to room temperature, as can be efficiently achieved with W-doping;[12,13] (ii) large solar transmittance modulation; and (iii) high luminous transmittance. Items (ii) and (iii) can be accomplished by antireflection in multilayer coatings[14–16] or, preferably, by nanothermochromics[17] embodying VO_2 nanoparticles dilutely embedded in dielectric hosts.[18,19] Doping with Mg is another approach to boost the luminous transmittance of VO_2 as experimentally discovered[20] and subsequently theoretically corroborated through hybrid-functional computations;[21] this doping also lowers τ_c.[20] Nanothermochromics with Mg-doped VO_2 was realized recently[22] and demonstrated improved luminous transmittance and additional benefits, of interest for practical fenestration, such as a less yellowish appearance. We are not aware of any prior, quantitative study on the effect of Mg-doping on the bandgap of VO_2, even though such information is essential for the design of Mg-doped VO_2-based materials. This paper reports a systematic study of VO_2 films with varying Mg contents and shows that a positive linear relationship can be established between bandgap and Mg content.

Thin films of Mg-doped VO_2 were prepared by reactive DC magnetron sputtering. The deposition chamber was initially evacuated to a base pressure of 6.3×10^{-7} millibars, and 80 ml/min of argon and 5 ml/min of oxygen (both 99.997%) were then introduced through mass-flow-controlled gas inlets; the total pressure was maintained at 1.2×10^{-2} millibars throughout the deposition. Co-sputtering was performed from 5-cm-diameter targets of vanadium (99.5%) at a power of 172 W and magnesium (99.9%) at a power of 0 to 57 W onto heated glass and carbon substrates kept at ~450 °C. More than 45 samples were grown to thicknesses of $40 < d < 87$ nm at a rate of ~0.06 nm/s. Some films from early depositions contained ~0.45 at. % of inadvertent Si as a systematic contamination. The value of d was determined with a Bruker DektakXT profilometer and was refined via optical analysis. Some of the as-deposited samples showed metallic properties and were post-annealed at ~450 °C in 1.3×10^{-2} millibars of oxygen for 15 to 60 min.

The elemental composition of the films deposited on carbon substrates were evaluated using Rutherford backscattering spectroscopy with 2 MeV ^{4}He ions backscattered at an angle of 170°. Specific data were obtained through iterative least-square fitting to experimental spectra using the SIMNRA program.[23] Figure 1 illustrates typical RBS data; panel (a) shows experimental and simulated spectra for a sample with an atom ratio $Mg/(Mg+V) \equiv z = 0.088$, and panel (b) reports corresponding data for a sample with $z = 0.079$ together with ~0.4 at. % Si. More than 30 samples were analyzed by RBS; more than 20 of these showed

a)Author to whom correspondence should be addressed. Electronic mail: Shuyi.Li@angstrom.uu.se.

 © 2013 AIP Publishing LLC

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.238.20.154 On: Wed, 23 Oct 2013 14:31:29

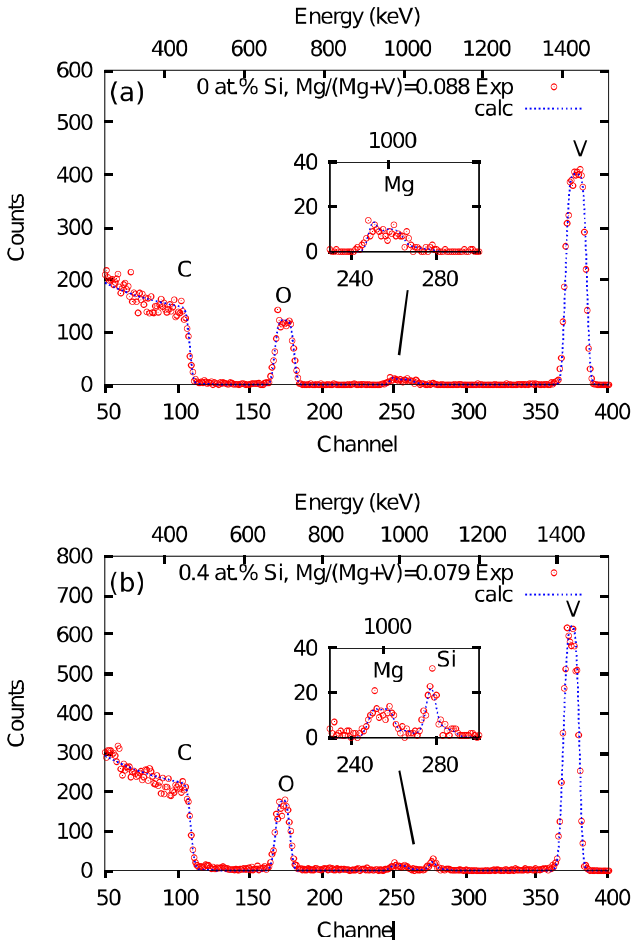


FIG. 1. Experimental and simulated RBS spectra for films with (a) an Mg/(Mg + V) atom ratio of 0.088 and (b) with Mg/(Mg + V) = 0.079 and additionally 0.4 at. % Si within the VO_2-based film. Insets show magnified data due to Mg and Si. In addition, evidence was found for an extremely thin, ~20 atomic layers thick, Si-rich accumulation layer between the VO_2-based film in (b) and the carbon substrate. This layer is considered to be insignificant for the optical analysis.

nothing but Mg doping, with $0 < z < 0.21$, whereas 11 samples had an additional Si content of $\sim 0.45 \pm 0.07$ at. %, in the Mg-doped vanadium oxide layer.

Spectral normal transmittance T and near-normal reflectance from the surface-coated side R_s and back side R_b of the samples were measured using a single-beam spectrophotometer devised for absolute measurements[24] and a Perkin–Elmer Lambda 900 double-beam spectrophotometer equipped with a $BaSO_4$-coated integrating sphere. Data were recorded in the wavelength range $300 < \lambda < 2500$ nm at room temperature and ~100 °C. Optical constants, n and k, were extracted by simultaneously fitting T, R_s, and R_b with

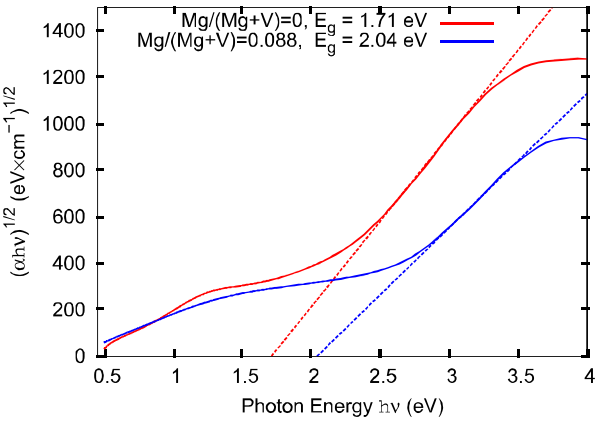


FIG. 3. $(\alpha h\nu)^{1/2}$ versus $h\nu$, where α is absorption coefficient and $h\nu$ is photon energy, with linear fittings to extract bandgap E_g at $\alpha = 0$. Data are reported for the shown values of the atom ratio Mg/(Mg + V).

simulated spectra computed from dielectric functions provided by oscillator models using commercial software[25] (below referred to as the "surface + back" method). Oscillator models for the semiconducting state of VO_2 contain four Brendel oscillators, two of which are located in the 1 to 2 eV (visible and near-infrared) range, one in the 3 to 4 eV range, and one further out in the ultraviolet. Models for the metallic state contain one Brendel oscillator in the 3 to 4 eV range, another Brendel oscillator in the near-infrared and, in addition, a Drude contribution for films with high conductivity. All of the oscillator models had a dielectric background contribution in the range of 2 to 5. Figure 2 shows experimental and fitted spectra for a pure VO_2 film and for an Mg-containing film with $z = 0.088$. Excellent agreement was found for the transmittance, as apparent from panel (c), whereas small discrepancies can be seen in the short-wavelength reflectance [cf. panels (a) and (b)], possibly caused by an inconsistency between R_s and R_b emanating from surface roughness. In order to suppress the influence from surface roughness, optical constants were evaluated also by fitting T and R_b ("back" method), which in general gave better agreement. For the Si-containing samples, optical constants were extracted by fitting R_s and T ("surface" method). Optical data suggested that samples with $z > 0.2$ tended to be non-thermochromic.

Optical absorption coefficients α were calculated from $\alpha = 4\pi k/\lambda$, and optical bandgaps E_g were then inferred via

$$(\alpha h\nu)^m = A(h\nu - E_g), \tag{1}$$

where $h\nu$ is photon energy, h is Planck's constant, and A is a constant.[26] The exponent m is 1/2, 1/3, 2, and 2/3 for

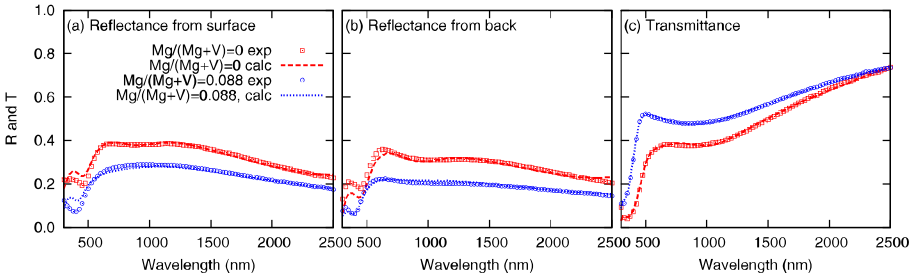


FIG. 2. Experimental and fitted spectral reflectance from (a) the surface-coated side R_s, (b) the back side R_b, and (c) for spectral transmittance T. Data are reported for the shown values of the atom ratio Mg/(Mg + V).

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.238.20.154 On: Wed, 23 Oct 2013 14:31:29

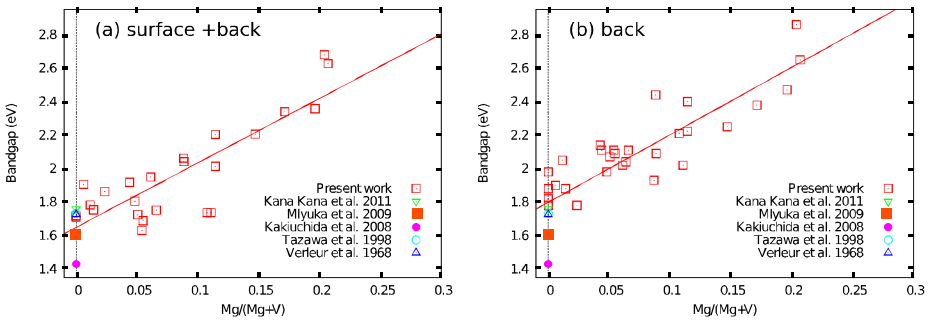


FIG. 4. Bandgap versus atom ratio Mg/(Mg + V) for Mg-doped VO_2 films. Data were evaluated from optical constants (a) obtained from fitting T, R_s, and R_b using the "surface + back" method and (b) obtained from fitting T and R_b using the "back" method. Literature data were obtained from Verleur *et al.*,[27] Tazawa *et al.*,[28] Kakiuchida *et al.*,[15] Mlyuka *et al.*,[16] and Kana Kana *et al.*[29]

indirect–allowed, indirect–forbidden, direct–allowed, and direct–forbidden optical transitions, respectively. The relationship $(\alpha h\nu)^m$ versus $h\nu$ can be fitted to a linear dependence near the onset of optical absorption, and E_g is then given by the intercept of this line and $\alpha = 0$. Assuming indirect–allowed transitions, two bandgaps can be extracted: at ~0.5 eV and at a value exceeding ~1.6 eV.[21,22] The larger bandgap is most relevant for the luminous transmittance and was investigated in this work; it has been assigned to transitions from predominantly O2p to V3d t_{2g} states.[13,21] Figure 3 shows examples of bandgap evaluations employing optical constants obtained from the "surface + back" method for samples with $z = 0$ and 0.088; the corresponding values of E_g were 1.71 and 2.04 eV, respectively. Bandgaps were extracted analogously also from optical constants available in the literature.[15,16,27–29]

Bandgap data were collected for in total 38 samples and were plotted as a function of Mg content. Figures 4(a) and 4(b) show results for the purely Mg-doped samples as obtained via the "surface + back" and "back" methods, respectively, as well as literature data.[15,16,27–29] The "back" method generally gave good fits to experimental optical spectra and hence yielded reliable bandgap values for all of our samples. However, the "back + surface" method sometimes produced inferior fits, and samples for which the deviations between experiment and calculations were unacceptable, according to the criteria in Ref. 25, were discarded in the optical bandgap analysis. Both plots show clear tendencies that can be captured by linear dependencies according to

$$E_g(z) = E_g(0) + \xi z, \tag{2}$$

with parameter values given in Table I. A small cluster of six data points with $0.05 < z < 0.12$ lie below the line in Fig. 4(a) but approximately on the line in Fig. 4(b). These results were obtained from samples that were metallic in as-deposited state and subjected to post-annealing in oxygen. This treatment might have caused sub-bandgap absorption. Nevertheless, the two values of ξ, given in Table I, are reassuringly similar and within each other's statistical error, which lends strong credence to our analysis.

TABLE I. Data for VO_2-based films with the shown doping and with optical constants evaluated by the indicated methods (cf. main text). $E_g(0)$ and ξ are parameters in Eq. (2).

Doping	Evaluation method	$E_g(0)$ (eV)	ξ (eV)
Mg	"Surface + back"	1.65 ± 0.04	3.85 ± 0.44
Mg	"Back"	1.80 ± 0.04	4.03 ± 0.39
Mg + Si	"Surface"	1.68 ± 0.04	7.05 ± 0.85

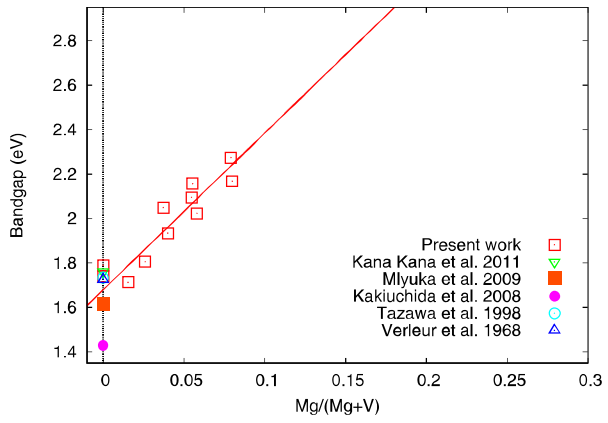


FIG. 5. Bandgaps versus atomic ratio Mg/(Mg + V) for (Mg,Si)-codoped VO_2 films with 0.45 ± 0.07 at. % of Si. Data were evaluated from optical constants obtained from fitting T and R_s using the "surface" method. Literature data were obtained from Verleur *et al.*,[27] Tazawa *et al.*,[28] Kakiuchida *et al.*,[15] Mlyuka *et al.*,[20] and Kana Kana *et al.*[29]

Figure 5 shows a corresponding plot for the Si-containing films evaluated by the "surface" method. Again the data fall along a line, determined by the parameters in Table I. The large magnitude of ξ is striking and shows an unambiguous effect of Si. However, the data are confined to films with $z < 0.1$, which is much smaller than for the samples reported on in Fig. 4, and we caution that further studies should be performed to ascertain the precise bandgap enhancement of Si-containing films.

In summary, we have carried out a thorough investigation on the quantitative influence of Mg-doping on the bandgap of thermochromic VO_2 films and shown that an unambiguous linear relationship can be established for films with or without the addition of a small amount of Si. The bandgap of purely Mg-doped films was found to increase by 3.9 ± 0.5 eV per unit of atom ratio Mg/(Mg + V). Furthermore, we report strong indications that this increase was even more pronounced for films with an additional, small amount of Si. Our data shed light on the enhanced luminous transmittance in Mg-doped VO_2 films, which is of large significance for thermochromic fenestration for energy efficient buildings.[11,30]

Financial support was received from the Swedish Research Council. We acknowledge assistance with RBS measurements from Pia C. Lansåker, P. Pettersson, and the staff of the Tandem Accelerator Laboratory at Uppsala University.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.238.20.154 On: Wed, 23 Oct 2013 14:31:29

[1]F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[2]J. H. Park, J. M. Coy, S. Kasiga, C. Huang, Z. Fei, S. Hunter, and D. H. Cobden, Nature **500**, 431 (2013).
[3]A. S. Belozerov, M. A. Korotin, V. I. Anisimov, and A. I. Poteryaev, Phys. Rev. B **85**, 045109 (2012).
[4]J. S. Lee, K. Shibuya, M. Kawasaki, and Y. Tokura, Phys. Rev. B **85**, 155110 (2012).
[5]C. Si, W. Xu, H. Wang, J. Zhou, A. Ablat, L. Zhang, J. Cheng, Z. Pan, L. Fan, C. Zou, and Z. Wu, Phys. Chem. Chem. Phys. **14**, 15021 (2012).
[6]Z. Tao, T. -R. T. Han, S. D. Mahanti, P. M. Duxbury, F. Yuan, and C.-Y. Ruan, Phys. Rev. Lett. **109**, 166406 (2012).
[7]X. Zhong, P. LeClair, S. K. Sarker, and A. Gupta, Phys. Rev. B **86**, 094114 (2012).
[8]C. B. Greenberg, Thin Solid Films **110**, 73 (1983).
[9]S. M. Babulanam, T. S. Eriksson, G. A. Niklasson, and C. G. Granqvist, Sol. Energy Mater. **16**, 347 (1987).
[10]M. Saeli, C. Piccirillo, I. P. Parkin, R. Binions, and I. Ridley, Energy Build. **42**, 1666 (2010); M. Saeli, C. Piccirillo, I. P. Parkin, I. Ridley, and R. Binions, Sol. Energy Mater. Sol. Cells **94**, 141 (2010).
[11]G. B. Smith and C. G. Granqvist, *Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment* (CRC Press, Boca Raton, FL, 2010).
[12]S.-Y. Li, G. A. Niklasson, and C. G. Granqvist, Thin Solid Films **520**, 3823 (2012).
[13]J. B. Goodenough, J. Solid State Chem. **3**, 490 (1971).
[14]P. Jin, G. Xu, M. Tazawa, and K. Yoshimura, Appl. Phys. A: Mater. Sci. Process. **77**, 455 (2003).
[15]H. Kakiuchida, P. Jin, and M. Tazawa, Sol. Energy Mater. Sol. Cells **92**, 1279 (2008).
[16]N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, Phys. Status Solidi A **206**, 2155 (2009).
[17]S.-Y. Li, G. A. Niklasson, and C. G. Granqvist, J. Appl. Phys. **108**, 063525 (2010); **109**, 113515 (2011); S.-Y. Li, K. Namura, M. Suzuki, G. A. Niklasson, and C. G. Granqvist, J. Appl. Phys. **114**, 033516 (2013).
[18]Y. Sun, S. Jiang, W. Bi, R. Long, X. Tan, C. Wu, S. Wei, and Y. Xie, Nanoscale **3**, 4394 (2011).
[19]Y. Gao, H. Luo, Z. Zhang, L. Kang, Z. Chen, J. Du, M. Kanehira, and C. Cao, Nano Energy **1**, 221 (2012); Y. Gao, S. Wang, H. Luo, L. Dai, C. Cao, Y. Liu, Z. Chen, and M. Kanehira, Energy Environ. Sci. **5**, 6104 (2012).
[20]N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, Appl. Phys. Lett. **95**, 171909 (2009).
[21]S. Hu, S.-Y. Li, R. Ahuja, C. G. Granqvist, K. Hermansson, G. A. Niklasson, and R. H. Scheicher, Appl. Phys. Lett. **101**, 201902 (2012).
[22]J. Zhou, Y. Gao, X. Liu, Z. Chen, L. Dai, C. Cao, H. Luo, M. Kanahira, C. Sun, and L. Yan, Phys. Chem. Chem. Phys. **15**, 7505 (2013).
[23]M. Mayer, AIP Conf. Proc. **475**, 541 (1999).
[24]P. Nostell, A. Roos, and D. Rönnow, Rev. Sci. Instrum. **70**, 2481 (1999).
[25]M. Theiss, *Hard- and Software for Optical Spectroscopy*, Manual for software SCOUT, Dr.-Bernhard-Klein-Str. 110, D-52078 Aachen, Germany, 2002, available at http://www.mtheiss.com. For fitting of optical data, we used the Downhill Simplex method, together with the stated criteria for acceptable fits, as described herein.
[26]F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).
[27]H. W. Verleur, A. S. Barker, Jr., and C. N. Berglund, Phys. Rev. **172**, 788 (1968).
[28]M. Tazawa, P. Jin, and S. Tanemura, Appl. Opt. **37**, 1858 (1998).
[29]J. B. Kana Kana, J. M. Ndjaka, G. Vignaud, A. Gibaud, and M. Maaza, Opt. Commun. **284**, 807 (2011).
[30]C. G. Granqvist, in *Nanotechnology for Eco-efficient Construction*, edited by F. Pacheco-Torgal, M. V. Diamanti, A. Nazari, and C. G. Granqvist (Woodhead, Cambridge, UK, 2013), pp. 236–269.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.238.20.154 On: Wed, 23 Oct 2013 14:31:29