

# Vanadium dioxide thermochromic opals grown by chemical vapour deposition

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Received 8 July 2008, accepted for publication 3 October 2008

Published 31 October 2008

Online at [stacks.iop.org/JOptA/10/125202](http://stacks.iop.org/JOptA/10/125202)

## Abstract

The semiconductor–metal transition that occurs in vanadium dioxide at 68 °C is the object of increasing interest in modern optics due to its applications in ultrafast optical devices. In a three-dimensional photonic crystal, the fine control of the structure is important for optimizing the switching magnitude and the spatial homogeneity. We report a controlled process to fabricate large-area high quality VO<sub>2</sub>–SiO<sub>2</sub> opals with fine control over the filling volume. The method comprises two stages. The first stage is a chemical vapour deposition synthesis whereby the vanadium pentoxide is grown. The second one is a thermal annealing that allows reducing the vanadium pentoxide to vanadium dioxide. We have carried out a steady-state study of the semiconductor–metal transition, for opals with the Bragg peak around the 1.55  $\mu\text{m}$  spectral region, by means of reflectance spectroscopy. As the temperature increases approaching the phase transition the intensity of the reflectance peak decreases and a small blueshift can be observed at 65 °C. When the phase transition is achieved at 68 °C the intensity of the reflectance peak decreases drastically and the Fabry–Perot oscillations disappear.

**Keywords:** opal, photonic crystal, VO<sub>2</sub>, thermochromism, phase transition

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Current interest in photonic crystals (PC) is primarily due to their proven potential in applications to control light propagation [1]. A photonic bandgap tunable through external stimuli would lead to their application in optical switches, tunable filters and optical interconnects/circuits. Fast control over the optical properties in the photonic crystal can be achieved by changing the refractive index of the constituent materials, which can be induced by several means, and can be a basis for the manipulation of light beams in PC on a subpicosecond timescale [2–4].

Vanadium dioxide is an object of increasing interest in modern optics due to its applications in ultrafast optical devices, at the nanoscale phenomena [5], in thin films [6–8] and photonic crystals [9–11]. The subpicosecond shifting of the photonic bandgap in a three-dimensional VO<sub>2</sub> opal photonic crystal has been demonstrated, controlled by a photoinduced semiconductor–metal phase transition [9, 10].

The feasibility of electrically programmable waveguiding in two-dimensional VO<sub>2</sub>-based PCs has been explored [12].

At room temperature, vanadium dioxide is a semiconductor material with monoclinic crystalline symmetry that transforms to a rutile metallic phase of tetragonal structure with a transition temperature  $T_c = 68^\circ\text{C}$  [13]. The phase transition is accompanied by strong changes in the dielectric constant with high transparency at the semiconductor phase and high reflectivity at the metallic phase in the broad frequency spectrum including the telecommunications window [14–16]. The semiconductor–metal (S–M) transition can be initiated not only by thermal excitation but also by photonic excitation or a high electric field, methods that produce an increase of carriers (Mott–Hubbard transition) [17]. Transitions of this type are, for example, found in transition metal oxides with partially filled bands near the Fermi level. Once the injected electron density reaches the critical value, the S–M transition is triggered and a metallic state is formed.

The analysis of the phase transition during the laser pulse in a 3D PC based on opal-vanadium dioxide shows that the fast

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phase transition (subpicoseconds) occurs in a limited fraction of opal pores filled with vanadium dioxide, while a picosecond temporal component reflects the spatial evolution of the phase boundary inside each pore. Thus, the fine control of the opal structure is important for optimizing the switching magnitude, the timescale and the spatial homogeneity.

The properties of vanadium oxides are strongly dependent on the stoichiometry, microstructure and crystallinity [18–20] which can be tailored by altering the deposition process parameters and the post-deposition thermal treatment. VO<sub>2</sub> thin films have been prepared from the atmospheric pressure chemical vapour deposition (CVD) reaction of VOCl<sub>3</sub> and H<sub>2</sub>O at reactor temperatures above 600 °C. In porous environments VO<sub>2</sub> has been synthesized within three-dimensional opal templates by the chemical bath deposition techniques, followed by thermal treatment at 800 °C [21], showing the opal Bragg peak in the visible range. Recently, preliminary results have been presented on these kinds of photonic crystals (visible range) prepared by atomic layer deposition at 490 °C, obtaining a material with a high content of V<sub>2</sub>O<sub>5</sub> and other sub-oxides due to the low growth temperature [22]. Vanadium pentoxide is a functional inorganic material having wide applications for such functions as gas sensors, catalysts and secondary battery electrodes. As an electrochromic material, it has reversible and persistent changes of the optical properties upon charging/discharging. Due to its limited optical modulation, V<sub>2</sub>O<sub>5</sub> films may be useful as a passive counter electrode in conjunction with an active working electrode in complementary electrochromic devices.

Here, we report a controlled process to fabricate large-area high quality VO<sub>2</sub>–SiO<sub>2</sub> opals with fine control over the filling volume by the CVD method. Techniques involving the gas phase are very useful in porous environments such as opals, as they are the most appropriate approach for conformal infiltration, which allows a perfect replication of the template and very precise control of the degree of infiltration, which, in terms of thickness, means nanometre-thick layers. We have carried out a steady-state study of the S–M transition for opals with the Bragg peak around the 1.55 μm spectral region. The thermochromic behaviour of VO<sub>2</sub> opals was observed at visible and near-infrared wavelengths.

## 2. Experimental details

### 2.1. Colloidal crystal template preparation

Silica particles (640 nm diameter) were produced by the standard Stöber method [23]. Prior to the assembly of the opal, silica spheres as dry powders were heat treated in order to prevent the appearance of cracks [24] in the opals during the subsequent dehydroxylation and infiltration processes; silica powder was treated at 600 °C at atmospheric pressure for 72 h. Silica spheres were arranged by the vertical deposition method [25] to form thin artificial opals, which were used as templates for further processing. Silicon was used as the substrate.

After growth, the opals were treated at 700 °C to remove the hydroxyl groups from the silica surface [26].

### 2.2. VO<sub>2</sub> opal preparation

The method to prepare VO<sub>2</sub>–SiO<sub>2</sub> opals comprises two well-differentiated stages. The first one is a CVD synthesis whereby the vanadium pentoxide is grown, and the second one is a thermal annealing that allows us to reduce the vanadium pentoxide to vanadium dioxide.

V<sub>2</sub>O<sub>5</sub> infiltration was performed following a CVD method based on a similar procedure described in the literature [27]. Water and triisopropoxyvanadium (V) oxide were used as precursors. The two sources were kept separate in glass bubblers, the water at room temperature and the triisopropoxyvanadium (V) oxide at 70 °C due to the high boiling point of this compound. The reactor containing the sample was kept at room temperature. The precursors were alternately fed into the reactor using nitrogen as the carrier gas (a cycle) at a fixed flow rate. By controlling the number of cycles (alternate exposure to the two sources in succession) it is possible to finely control the degree of infiltration in silica opals and thus the optical behaviour of the samples. This fact is important in order to tune the photonic properties to the desired specifications for optimal performance. Due to the conformal growth and geometrical constraints the maximum value achievable for the filling fraction is close to 86% of the pore volume. The conversion to VO<sub>2</sub> from V<sub>2</sub>O<sub>5</sub> reduces the maximum filling fraction to 61% because of the higher density of VO<sub>2</sub> (4.34 g cm<sup>−3</sup> for VO<sub>2</sub> against 3.35 g cm<sup>−3</sup> for V<sub>2</sub>O<sub>5</sub>).

For the reduction processing the V<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub> opals were placed inside a quartz ampoule closed under high vacuum (5 × 10<sup>−6</sup> Torr). The ampoule was then ramped at 100 °C h<sup>−1</sup> up to the annealing temperature (set at temperatures from 400 to 700 °C) and kept at that temperature for 6 h.

Inverse opals were obtained by etching with HF (1 wt%) of silica, once the VO<sub>2</sub> was obtained. This process completely removes the silica matrix.

Optical spectroscopy has been performed in order to monitor the infiltration process and x-ray diffraction to analyse the crystal quality and composition of the samples.

### 2.3. Characterization

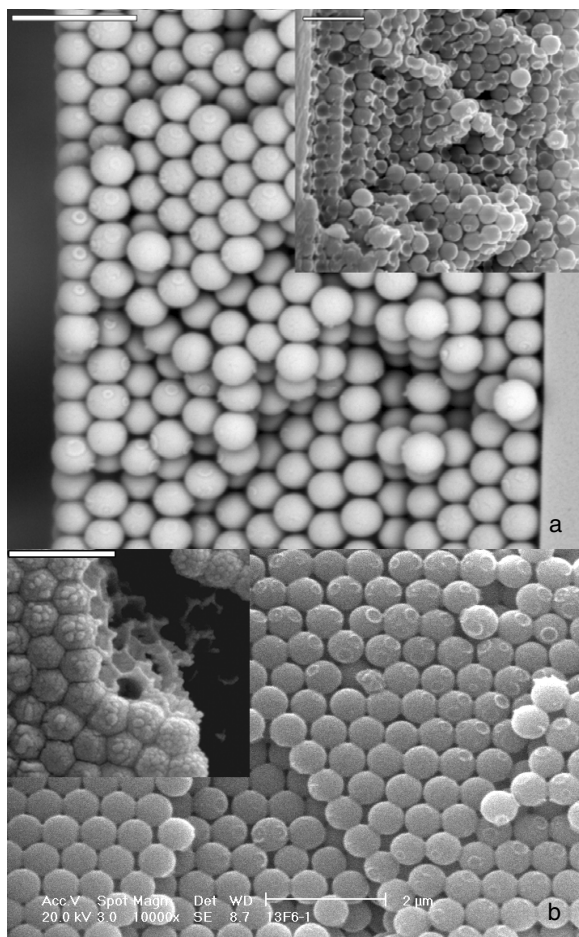
The glancing x-ray diffraction study was carried out in a PANalytical BV X'PERT PRO MRD using Cu Kα radiation. The x-ray powder diffraction study at different temperatures was carried out in a PANalytical BV X'PERT PRO MPD.

The SEM images were taken in a Zeiss DSM 960 and a Philips XL 30.

Optical characterization was performed in a Fourier-transform infrared spectrometer, IFS 66S from Bruker, with an IR microscope attached. All reflectance spectra were recorded at near-normal incidence to the (111) family of planes. All compared spectra were taken at the same sample spot. The sample was heated by a resistance heater and temperature was measured by a thermocouple.

## 3. Results and discussion

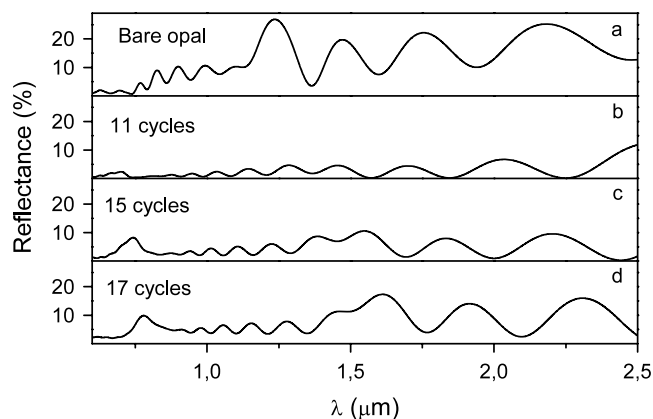
Figure 1 shows SEM images of V<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub> opals and VO<sub>2</sub> opals grown on silicon substrates with different degrees of



**Figure 1.** (a) SEM image of cleaved edges of a  $V_2O_5$ - $SiO_2$  composite opal obtained after 6 infiltration cycles. The inset shows the  $V_2O_5$ - $SiO_2$  composite opal after 20 cycles. (b) SEM image of a  $VO_2$ - $SiO_2$  composite opal obtained after 6 infiltration cycles. The inset shows the  $VO_2$  inverse opal after 20 cycles. The opals were made with 610 nm silica particles. Scale bars are 2  $\mu m$ .

infiltration. The images show the appearance of a cleaved edge of  $V_2O_5$ - $SiO_2$  composites obtained after 6 (figure 1(a)) and 20 infilling cycles (inset in figure 1(a)). Since the dielectric constant of the amorphous  $V_2O_5$  growth in these samples is not accurately determined it was not possible to estimate the filling fraction. These images show the homogeneous and conformational growth of  $V_2O_5$  on the silica particles and also the different thicknesses of the shells for the two different infilling processes. It is observed that the filling fraction is low even after 6 infilling cycles. Figure 1(b) shows images of  $VO_2$  opals obtained after an annealing process at 500 °C under vacuum. The main figure 1(b) corresponds to a  $VO_2$ - $SiO_2$  composite opal obtained after 6 infilling cycles and the inset shows the  $VO_2$  inverse opal obtained after 20 infilling cycles. The silica particles were removed using HF at 1 wt%. In these images a smooth  $VO_2$  is observed recovering for a low filling fraction opal (figure 1(b)) and a roughness  $VO_2$  when the filling fraction is high.

The slow infilling process allows a fine control of the opal filling fraction. This infilling process has been monitored by the optical reflectance at near-normal incidence with respect to

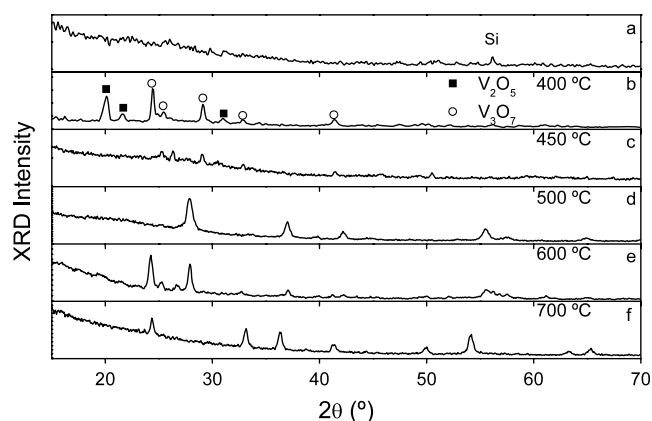


**Figure 2.** Reflectance spectra for bare silica opal (a) and three different infilling steps. The Bragg peak shifts to higher wavelengths as the  $V_2O_5$  content increases. Notice the Fabry-Perot ripples due to the opal thin film thickness (in this case around 4  $\mu m$ ).

the (111) face-centred cubic (fcc) planes taken with the help of an optical microscope and spectrometer. Figure 2 shows the reflectance spectra for the bare opal and three infilling process stages. The bare silica opal (figure 2(a)) spectrum shows a peak centred at 1237 nm, corresponding to the first photonic pseudogap opening at point L of the Brillouin zone. Since the opals are very thin, Fabry-Perot oscillations can be seen along with the stronger Bragg peak. After 11 cycles (figure 2(b)) the Bragg peak has all but disappeared. This is due to the average refractive index of the pore ( $V_2O_5$ /air) which reaches that of the silica backbone, producing an index-matching effect that hides the Bragg peak: a system consisting of a homogenized thin layer is achieved where only Fabry-Perot oscillations are observed. At lower wavelengths, however, a hint of the higher energy features is already visible which guarantees that 3D periodicity and high quality are still present [28]. These peaks, unlike the Bragg peak that signal only the vertical stacking, are an unequivocal signature of lateral periodicity and stacking order [29]. In figure 2(c) (after 15 infiltration cycles) the Bragg peak can be observed to reappear at higher wavelengths and after 17 cycles (figure 2(d)) the peak is centred at 1614 nm owing to the increase of the average refractive index of the structure due to the high  $V_2O_5$  content. High energy features are reinforced and clearly visible now.

The existence of a large number of distinct vanadium oxide phases with different crystal structures, including polymorphs of  $VO_2$  and the Magneli phases ( $V_nO_{2n-1}$  for  $n = 3-9$ ), and separated from each other by subtle changes in the partial pressure of oxygen and/or temperature, implies that the phase(s) of vanadium oxide obtained are very sensitive to the deposition process parameters and/or the post-deposition thermal treatment [30, 31].

During CVD synthesis the reactor was kept at room temperature and the as-grown  $V_2O_5$  layers are amorphous, as observed by x-ray diffraction (XRD). The  $V_2O_5$ - $SiO_2$  opals were treated at different temperatures, from 400 to 700 °C under vacuum ( $5 \times 10^{-6}$  Torr), to study the  $V_2O_5$  reduction process. The glancing-angle XRD data are shown in figure 3. Figure 3(a) shows the as-grown sample amorphous state. In



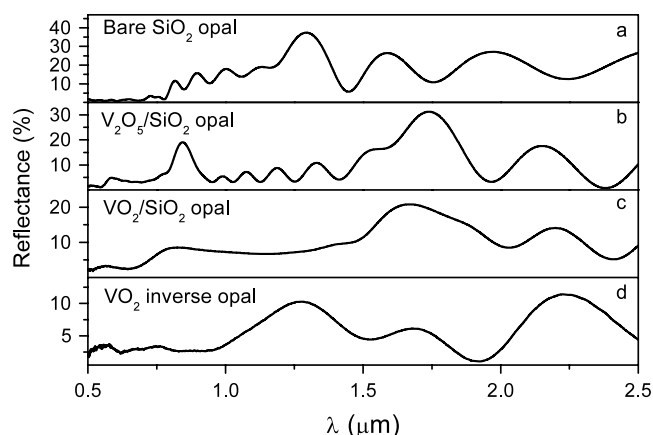
**Figure 3.** From top to bottom: glancing XRD diffractograms from as-grown  $V_2O_5$ - $SiO_2$  opal and after 5 different thermal treatments.

this figure only the Si peak corresponding to the sample substrate can be observed. The sample heated at 400 °C for 6 h (figure 3(b)) shows diffraction peaks corresponding to  $V_2O_5$  and  $V_3O_7$ . This indicates the beginning of the reduction process that, according to the literature, follows the sequence  $V_2O_5$ - $V_3O_7$ - $V_4O_9$ - $V_6O_{13}$ - $VO_2$  [30]. The XRD spectrum of the sample treated at 450 °C for 6 h shows low intensity peaks (figure 3(c)). At this annealing temperature the  $V_2O_5$  peaks have disappeared and the intensity of the  $V_3O_7$  peaks has decreased while those corresponding to  $V_4O_9$ ,  $V_6O_{13}$  and  $VO_2$  (B and M phases) start to appear. The more intense peaks correspond to  $VO_2$  (B) and  $V_4O_9$ .  $VO_2$  (B) is a metastable phase which can convert into stable  $VO_2$  (M) by annealing [31]. While  $VO_2$  (B) and  $VO_2$  (M) belong to the monoclinic system they have different space groups:  $C2/m$  for  $VO_2$  (B) and  $P21/c$  for  $VO_2$  (M). When the  $V_2O_5$ - $SiO_2$  opals are heated at 500 °C the complete conversion to  $VO_2$  (M) is observed (figure 3(d)). For thermal treatment at 600 °C a mixture of  $VO_2$  and  $V_2O_3$  can be observed in XRD spectra (figure 3(e)). Further thermal treatments at higher temperature reduce the  $V_2O_5$  to  $V_2O_3$ , as shown in figure 3(f) for 700 °C. Therefore the treatment at 500 °C is adopted as the most appropriate.

The  $VO_2$  (M) grain size was found to change with infiltration increasing from 14 to 22 nm for  $VO_2$ - $SiO_2$  opals with 10 and 17 cycles of infilling, respectively.

The process of reduction to  $VO_2$  can again be monitored by optical spectroscopy. In figure 4 four reflectance spectra are shown, which correspond to bare silica opal (figure 4(a)); composite  $V_2O_5$ - $SiO_2$  opal after 20 cycles of infilling (figure 4(b)); composite  $VO_2$ - $SiO_2$  opal after annealing at 500 °C at reduced pressure (figure 4(c)); and  $VO_2$  inverse opal after etching of silica with hydrofluoric acid (figure 4(d)). From spectra 4c and 4d the filling fraction was estimated as about 55% by comparing these spectra with photonic band calculations performed using the MPB program and considering 8.8 as the dielectric constant of  $VO_2$ .

As expected, the Bragg peak centred at 1237 nm for the bare silica opal shifts to higher wavelength after  $V_2O_5$  infiltration. After the reduction process, this peak moves, if at all, to slightly lower wavelengths although the dielectric



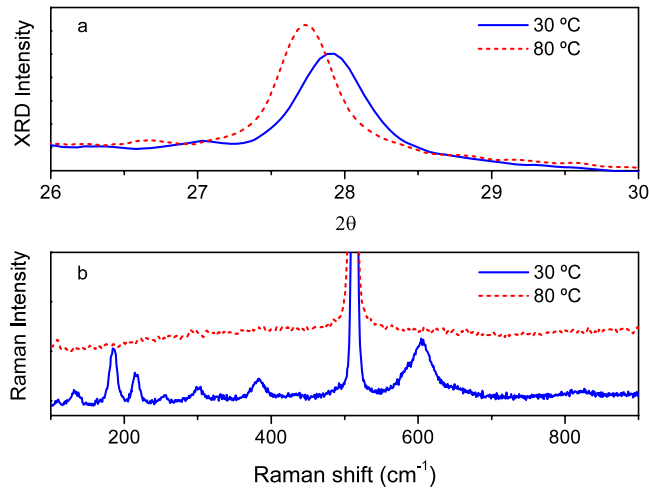
**Figure 4.** Reflectance for the bare silica opal (a),  $V_2O_5$ - $SiO_2$  composite (b),  $VO_2$ - $SiO_2$  composite (c) and  $VO_2$  inverse opal (d).

constant of  $VO_2$  is higher than that of  $V_2O_5$ . This is due to a lower pore filling fraction arising from a higher density of  $VO_2$  that compensates for the refractive index. As is observed in the inset of figure 1(b) the reduction process converts the smooth  $V_2O_5$  to rough  $VO_2$  and for this reason the reflectance decreases and the high energy features smear, as is observed in figure 4(c). After chemical etching of silica, the peak shifts even further down to lower wavelengths due to lower average refractive index.

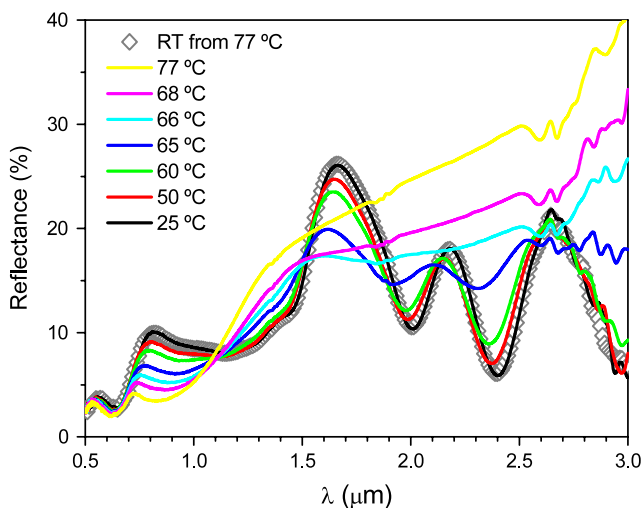
The thermochromic phase transition was studied by XRD and Raman spectroscopy. X-ray diffraction shows a structural phase transition from monoclinic to tetragonal rutile  $VO_2$ . Figure 5(a) shows a shifted x-ray diffraction pattern for the *in situ* heated sample. It is apparent that the diffraction peak at  $2\theta = 27.95^\circ$  corresponding to monoclinic  $VO_2$  (M) (011) at temperatures of 30 °C shifts to a lower angle of  $2\theta = 27.73^\circ$  at the higher temperature of 80 °C (well above the phase transition temperature) with a slight increase of the diffraction intensity. This shifted diffraction peak is considered to originate from tetragonal  $VO_2$  (110), which results from distortion of the monoclinic  $VO_2$  (M) (011) plane [32]. Figure 5(b) shows the Raman spectra from the  $VO_2$ - $SiO_2$  opal at two different temperatures. The spectrum at 30 °C shows the frequencies of the phonon lines associated with  $VO_2$  (M) and a sharp, intense peak corresponding to the Si substrate. On the other hand, the spectrum taken at 80 °C only shows the peak corresponding to the Si substrate. This is indicative of the emergence of that metallic phase where no phonons are detected. On cooling back to 30 °C the spectrum of monoclinic  $VO_2$  reappeared. This illustrates the reversibility of the S-M transition.

The thermochromic phase transition was also monitored by optical spectroscopy. Figure 6 presents the reflectance spectra from the (111) surface at normal light incidence of the  $VO_2$ - $SiO_2$  composite opal. The spectra were measured at temperature below, around and above the phase transition temperature. The phase transition in  $VO_2$  changes its dielectric constant and thus the average dielectric constant of the composite opal.

As the temperature increases approaching the phase transition the intensity of the reflectance peak (at 1662 nm)



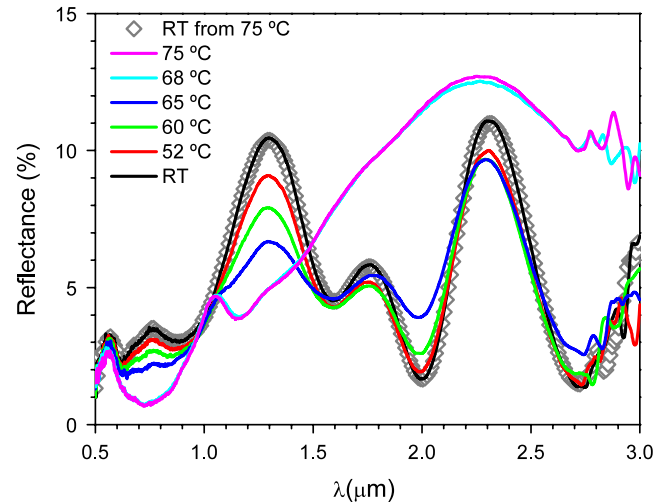
**Figure 5.** X-ray diffraction patterns (a) and Raman spectra (b) for the *in situ* heated VO<sub>2</sub>-SiO<sub>2</sub> opal. Respective sample temperatures before and after heating were 30 and 80 °C.



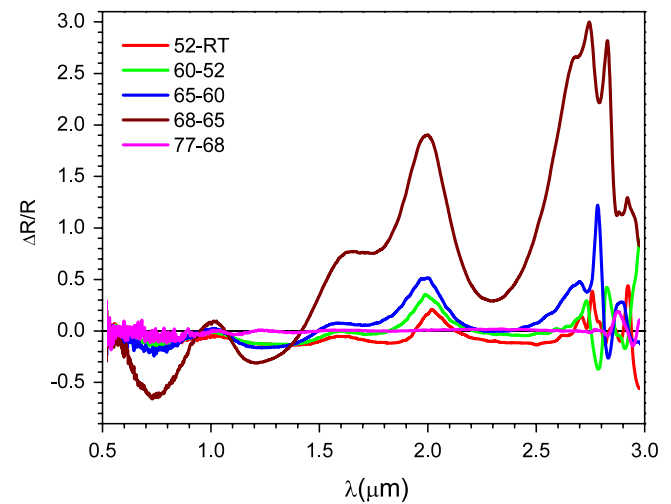
**Figure 6.** Reflection spectra from the (111) surface of the VO<sub>2</sub>-SiO<sub>2</sub> composite opal at different temperatures including a spectrum taken after cooling back down to room temperature.

decreases and a small blueshift can be observed at 65 °C. When the phase transition is achieved at 68 °C the optical response changes drastically. The Fabry-Perot oscillations due to the sample's finite size disappear and a broad peak can be observed at 1618 nm. For temperatures higher than the phase transition a strong increment of the reflectance is observed for wavelengths higher than 1.5 μm. This behaviour shows the metallic nature of the VO<sub>2</sub> high temperature phase [14]. On cooling, the initial RT spectrum is recovered, as can be seen in figure 6. This proves that cyclability is ensured.

The same optical study as a function of temperature was carried out for the VO<sub>2</sub> inverse opal (see figure 7). The inverse structure presents a reflectance peak at higher energy than the composite opal due to the lower average dielectric constant. As in the case of the composite opals, as the temperature increases the intensity of the Bragg peak (at 1294 nm for this inverse structure) decreases. The peak position does not change much



**Figure 7.** Reflectance spectra from the (111) surface of the VO<sub>2</sub> inverse opal at different temperatures.



**Figure 8.** Thermal differential reflectance spectra obtained from figure 7.

even at 65 °C. The drastic change in the reflectivity for temperatures higher than 68 °C shows the different behaviour of the semiconductor and metallic phases of the VO<sub>2</sub> inverse opal. The entrance of the metallic phase with a strongly varying complex dielectric function complicates the spectrum that presents a new peak centred at 1055 nm and the onset of a high reflectance at IR wavelengths in compliance with the metallic nature of the structure. Furthermore, the formation of the metallic state results in the appearance of surface-plasmon resonances in the near-infrared spectral region [33, 34].

In order to make the thermal tunability more patent, figure 8 displays the differential reflectance obtained from figure 6 by taking the difference between successive spectra. As can be seen, differences between spectra at temperatures away from that of the phase transition weakly oscillate around zero; however, near the transition large oscillations can be appreciated. It can be seen that differential reflectance is mostly negative in the Bragg peak and positive in the

absorption region of the metallic phase. In regions where Fabry–Perot oscillations yield negligible reflectance in the dielectric structure huge peaks of several hundred per cent increase are obtained. Considering that differences of a few per cent are significant and can be considered more than sufficient in many devices the measured differences seen this case are enormous in terms of applications, especially for sensors.

The effects brought about by the changes in dielectric function are greater in the infrared because of the phase transition but those in the VIS are also appreciable and can even be noticed in the second order (below 1  $\mu\text{m}$ ). Actually only those features below 1  $\mu\text{m}$  represent 3D effects since those associated with the longer wavelengths originate from the periodic vertical stacking and reflect the one-dimensional character of the system. It is expected that, to fully exploit the potential of these structures, changes in the higher energy range should be studied.

#### 4. Conclusions

In summary, we report here the use of CVD and thermal annealing to grow  $\text{VO}_2\text{--SiO}_2$  composite and  $\text{VO}_2$  inverse opals. This method yields large-area, high quality  $\text{VO}_2\text{--SiO}_2$  structures and is based on the growth of  $\text{V}_2\text{O}_5$  and later annealing under vacuum. It is shown that thermal treatment under reduced pressure transforms the  $\text{V}_2\text{O}_5$  to  $\text{VO}_2$  with good control of stoichiometry. The thermochromic behaviour has been shown for both  $\text{VO}_2\text{--silica}$  composites and  $\text{VO}_2$  inverse opals through different techniques. The photonic bandgap behaviour is shown to be strongly affected by the phase change and holds promise for photonic devices operated either optically, electrically or thermally.

#### Acknowledgments

This work was partially funded by the Spanish Ministry of Science and Education under contracts MAT2006-09062 and NAN2004-08843, and the EU under contract IST-511616 NoE PhOREMOST. MI is a Ramón y Cajal researcher. This work used the Electronic Microscopy facility at the Centro de Ciencias Medioambientales (CSIC) and the x-ray diffraction facility at the Universidad Complutense de Madrid.

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