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Intelligent window coatings: atmospheric pressure chemical vapour deposition of vanadium oxides

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Thin films of the vanadium oxides, V_2O_5, VO_2, VO_x ($x = 2.00$–2.50) and V_6O_{13} were prepared on glass substrates by atmospheric pressure chemical vapour deposition (APCVD) of vanadium tetrachloride and water at 400–550 °C. The specific phase deposited was found to be dependent on the substrate temperature and the reagent concentrations. The films were characterised by Raman microscopy, X-ray diffraction (XRD), Rutherford backscattering (RBS), scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDX), reflectance/transmittance and UV absorption spectroscopy. The VO_2 films show by Raman microscopy and reflectance/transmittance spectroscopy, reversible switching behaviour at 68 °C associated with a phase change from monoclinic (MoO_2 structure) to tetragonal (TiO_2, rutile structure).

Introduction

Intelligent window coatings are those which can respond in a desired way to an external stimulus. These included heat-control coatings which are materials that can change their reflectance and transmittance properties with temperature. Since the late 1950's it has been known that single crystals of vanadium(IV) oxide undergo a reversible thermochromic transition at 68 °C.[1] The transition involves a monoclinic (MoO_2) to tetragonal (TiO_2 rutile) phase transformation, and is accompanied by a dramatic increase in electrical conductivity and infrared reflectivity. The phase change is associated with a displacement of 0.43 Å of sheets of vanadium atoms, such that in the monoclinic phase the vanadium d-electrons are localised to form V(IV)–V(IV) pairs within the chains,[2] whilst in the tetragonal phase these electrons are released into a conduction band. The change from semiconductor to semimetal properties makes VO_2 an ideal candidate for intelligent window coatings.[3]

Atmospheric pressure chemical vapour deposition (APCVD) is a good method for applying thin films to glass substrates. The process has the advantage of being easily integrated into float-glass production lines and has fast deposition rates. Vandium(IV) oxide thin films have been prepared by physical vapour deposition methods,[4] sol–gel and dip/spin coating.[5]

Chemical vapour deposition methods have been reported for the formation of vanadium oxide films. These include use of vanadium alkoxides,[5] $V(acac)_3$[6] and various oxovanadium reagents as precursors.[7] In these studies films were formed that contained mixed phases of vanadium oxides such as V_3O_7 and V_6O_{13} along with VO_2. Post treatment of these films by annealing in air encouraged the formation of nearly single phase VO_2. No literature was found referring to the use of VCl_4 to prepare VO_2. Vanadium(IV) chloride has been used to prepare V_2O_5 by the reaction of VCl_4 and a co-oxygen source such as methanol and ethanol but the films were contaminated with carbon.[8] Vanadium(V) oxide films have been post-reduced to vanadium(IV) oxide by heating in a reducing atmosphere.[5]

This paper details the production of vanadium oxide films from the APCVD of VCl_4 and water. It was found possible to isolate a range of different vanadium oxide phases by control of the temperature and the concentrations of the gaseous reagents in the reactions. In particular, vanadium(IV) oxide thin films could be made by APCVD without requiring post-treatment reduction.

Experimental

Chemical vapour deposition studies

All APCVD experiments were performed on a custom built apparatus consisting of a horizontal-bed cold-wall reactor connected to an arrangement of stainless-steel heated pipes, valves and bubblers. A syringe driver was attached to the plain-line gas-flow for the introduction of water. A schematic of the APCVD rig used is shown in Fig. 1. All heaters were regulated by Eurotherm controllers and RS type k thermocouples.

Vanadium(IV) chloride (Aldrich, UK, 99%) was transferred to bubbler 2 and distilled water was injected into the plain-line gas-flow using a fixed-rate syringe driver (1.33 cm min^{-1}). The amount of water introduced was controlled *via* the size of the syringe. The substrate was SiO_2-precoated standard float

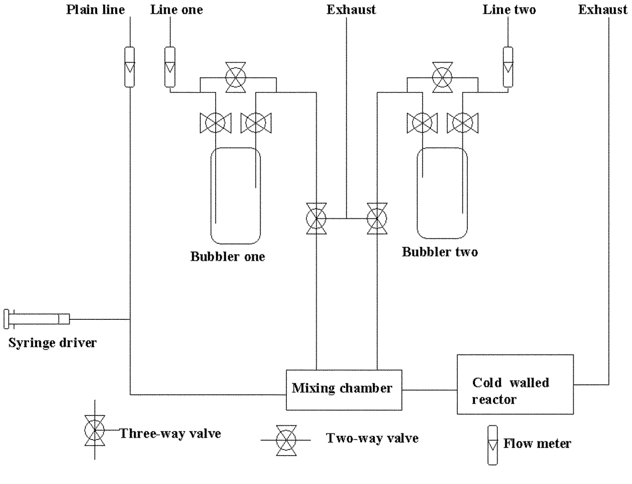

Fig. 1 Schematic representation of the APCVD rig.

glass (Pilkington, UK) 15 cm × 4.5 cm × 0.3 cm. The glass substrate was cleaned before use by being wiped with a tissue soaked in water, then with a tissue soaked in propan-2-ol and finally rinsed with propan-2-ol. The glass was allowed to dry in air prior to its being mounted in the CVD chamber.

A series of films was produced in which the precursor ratio was kept constant at 1 : 10 VCl_4 : H_2O and the substrate temperature varied between 350 and 550 °C. Another series of films was produced in which the VCl_4 : H_2O ratio was varied at a constant substrate temperature of 550 °C.

A flow of nitrogen (BOC, 99.99%) was passed through the apparatus during all operations of the APCVD rig. The plain-line flow was typically 1.1 L min^{-1} and that through bubbler 2 was 0.2 L min^{-1} for the variable substrate temperature studies. The amount of VCl_4 introduced into the system was calculated from $a = (VP/F)/((760 - VP)/24.4)$, where a is the amount of material introduced (mol min^{-1}), VP is the vapour pressure of the material at the temperature of the bubbler (mmHg), and F is the carrier-gas flow-rate through the bubbler (L min^{-1}).

Once all temperatures had stabilised, the syringe driver valve was opened and distilled water was introduced into the plain-line gas-flow. Nitrogen was passed through the bubbler and the bypass valve was closed. Vanadium(IV) chloride was seen to pass through the exhaust. After allowing the flow to stabilise for approximately 10–20 s the three-way valve was switched to allow the precursor to pass into the mixing chamber and on to the reactor. Once the allotted reaction time was complete the three-way valve was switched to the exhaust, the bypass valve opened and the nitrogen flow through the bubbler closed. The reactor heater was turned off and the substrate allowed to cool under an atmosphere of nitrogen. The substrate was removed from the reactor below 200 °C. All samples were handled and stored in air.

Film analysis

Analysis of the resulting films consisted of UV/visible absorption spectroscopy, contact angle measurements, scratch tests, solubility tests, photocatalysis measurements, visible/IR reflectance/transmittance and Raman spectroscopy, SEM/EDX and glancing angle X-ray diffraction. X-Ray analysis of the films was determined using glancing angle incidence (1.5°) on a Siemens D5000 machine using primary monochromated Cu-$K_{\alpha 1}$ radiation (1.5406 Å). SEM/EDX was determined on a JEOL 35-CF instrument using ISIS software (Oxford Intruments). Electronic absorption measurements were obtained using a Thermospectronic Helios-α spectrometer from 300–1100 nm. Reflectance/transmittance measurements were made on a Zeiss miniature monolithic spectrometer (range 380–1150 nm) connected to a PC.[8] Sheet resistances were determined on a four-probe instrument. Raman measurments were carried out using a Renishaw System 1000 Raman spectrometer with a HeNe (632.8 nm) laser excitation source. The temperature of the sample was controlled by a Linkam THMS600 variable temperature cell with a liquid nitrogen pump. Rutherford backscattered spectra were obtained using a 2 MeV accelerator, the analysing beam was 2 MeV He^+ with the sample being analysed at normal incidence with a scattering angle of 168° in IBM geometry. Quark software was used for the simulation. Contact angles of selected glass samples were determined by measuring the spread of a 1.0 μL droplet of water. Scratch tests were determined with a paper towel, brass stylus and stainless steel scalpel. Solubility tests were achieved by immersion of small pieces of the coated glass in a range of solvents (toluene, acetone, methanol, hexane, water, 2 M NaOH, 2 M HCl and 2 M HNO_3). Adhesion of the films to the substrate were determined by the Scotch tape test (removal of an X shaped piece of sticking tape).

Photocatalytic analysis

Photocatalysis of the samples was assessed by the destruction of an overlayer of a test organic – stearic acid – on a 3 cm × 3 cm portion of glass coated with VO_2. This coated glass had been irradiated at 254 nm for 1 h prior to measurement. The stearic acid was applied by dropping 7.5 μL of a 0.4 mmol methanol solution onto the glass surface, which was spun at 1500 revolutions a minute during the dropping procedure. The infrared spectra of the stearic acid overlayer was measured over the range 2950–2800 cm^{-1}. The glass coated with stearic acid was irradiated with 254 nm radiation provided by BDH germicidal lamps (2 × 8 W). The IR spectra of the stearic acid were measured after 30 min intervals for up to 2 h and the areas of the bands attributed to the C–H stretches quantified.

Results and discussion

Synthesis

Reaction of vanadium tetrachloride with water under APCVD conditions leads to a range of vanadium oxide coatings on glass substrates; VO_2, VO_x, V_6O_{13} and V_2O_5. The specific phase of vanadium oxide produced in the CVD experiments was determined by two variables; the ratio of VCl_4 to water in the gas stream and the temperature of the substrate. No films could be grown at a substrate temperature of below 400 °C. From 450-475 °C at a constant ratio of 10 : 1 H_2O to VCl_4 only V_2O_5 was obtained. At 500 °C and above, with a 10 : 1 ratio, VO_2 was obtained. This indicates that higher temperatures promote the formation of a less oxygen-rich phase. At 550 °C changes in the ratios of water to VCl_4 had a profound effect on the composition of the vanadium oxide film deposited. At a ratio of 57 : 1 to 7 : 1 H_2O to VCl_4, VO_2 was obtained, at a ratio of 6 : 1 until 4 : 1 VO_x films ($x = 2.0$–2.5) were obtained and at 3 : 1 H_2O to VCl_4, V_6O_{13} films were obtained. It was noted on a number of the samples that the edges of the films (*ca* 0.5 cm) had a different composition from that of the bulk of the film. At no point were two phases observed to coexist in the same portion of the film.

Characterisation

The films produced in the APCVD reaction of VCl_4 and water were yellow, adhesive and they passed the Scotch tape test. They were insoluble in water and common organic solvents, but they did readily dissolve in both dilute acid and alkali (2 M). Solubility in acid and alkali is a feature of bulk solid-state vanadium oxide chemistry.[9] Higher flow rates of the inert N_2 carrier gas also led to better film uniformity, adhesion and coverage over the whole substrate surface. Higher flow rates also prevented blockages, caused by pre-reaction of the precursors prior to entering the coater chamber (Table 1). By changing the coating time, the thickness of the films could be altered, typical growth rates being *ca* 0.5 μm min^{-1} at 550 °C. Typical film thickness were 0.5 to 1.5 μm.

Raman microscopy proved to be an extremely useful tool for the analysis of the films, Fig. 2, there being four different vanadium oxide phases identified. Raman patterns were obtained at various points on the surfaces of the coatings. It was noted that at all points analysed only a single phase was detected. The predominant phase identified in these studies was monoclinic VO_2 which showed bands at 143, 192, 223, 261, 310, 390, 500 and 612 cm^{-1} (Fig. 2a). Notably no bands due to VO_2(B), the metastable form of VO_2 first identified by Theobald[10] were observed. Parker[11] and independently Aronov[12] identified Raman bands for monoclinic VO_2 at 143, 191, 223, 262, 310, 389, 497 and 611 cm^{-1}. They assigned these bands to A_g modes with the exception of that at 143 cm^{-1} which was not assigned. The 611 cm^{-1} band is due to a V–O stretching mode.

Table 1 Experimental conditions established for the APCVD reaction of VCl_4 and H_2O and the compositions of the vanadium oxides formed

VCl_4 to H_2O ratio	Substrate temperature/°C	Composition^a
1 : 57	550	VO_2^b
1 : 52	550	VO_2^b
1 : 20	550	VO_2^b
1 : 7	550	VO_2
1 : 6	550	VO_x
1 : 4	550	VO_x (V_6O_{13})
1 : 3	550	V_6O_{13}
1 : 10	400	No film
1 : 10	450	V_2O_5
1 : 10	475	$V_2O_5^b$
1 : 10	500	VO_2^b
1 : 10	550	VO_2^a

^{a}From Raman and X-ray diffraction measurements. ^{b}A secondary phase of VO_x formed on the colder edges of the glass substrates either at the leading edge (*ca* 0.5 cm) or the side edge (*ca* 0.5 cm) of the coating. In no deposition were the VO_x and the primary phase observed to coexist in the same portion of the substrate.

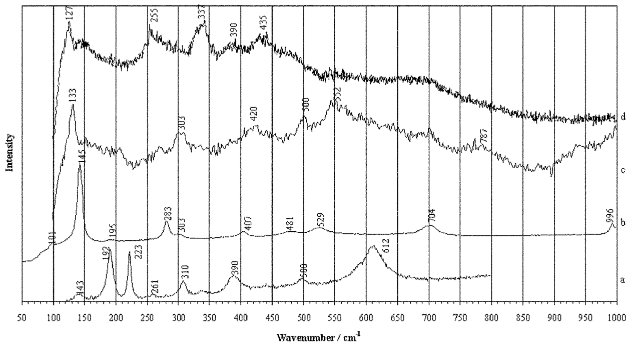

Fig. 2 Representative Raman spectra of a) VO_2, b) V_2O_5, c) V_6O_{13} and d) VO_x formed from the APCVD reaction of H_2O and VCl_4 (λ_0 = 632.8 nm, power = 2 mW).

The Raman spectra of V_2O_5 (Fig. 2b) showed bands at 145, 195, 283, 303, 407, 481, 529, 704 and 996 cm^{-1} which matched those previously reported for thin films and from microcrystalline powders both in the wavenumber and intensity.[13] The intense narrow band at 145 cm^{-1} is due to vibrations of the –V–O–V– atoms. The band at 996 cm^{-1} is characteristic of the V=O stretch.

The Raman spectra of the V_6O_{13} films (Fig. 2c) showed bands at 133, 303, 420, 500, 552 and 787 cm^{-1}, which match extremely well those of powdered V_6O_{13}[14] and RF magnetron-sputtered V_6O_{13} films.[15] By comparison with previous work the band at 787 cm^{-1} is assigned to a bridging V–O bond stretch, the 552, 501 and 420 cm^{-1} bands to V–O–V stretches and the 303 and 131 cm^{-1} bands to external modes. The most intense band in the Raman spectrum of V_6O_{13} has been measured at 139 cm^{-1} for a single crystal, 137 cm^{-1} for a powdered sample and at 132 cm^{-1} for RF sputtered thin films. In this study the most intense band was at 131 cm^{-1}. Wang has shown[16] that the shift in wavenumber of this band can be related to the crystallite size of V_6O_{13} which, for the material prepared in this study is comparable to that (350 Å) of RF sputtered films.

The Raman spectra of the VO_x phase (Fig. 2d) matched that reported by Barecca.[7] This material has an ill defined stoichiometry and is actually a collection of VO_x (x = 2.0–2.5) phases which have very similar structures and which are interconverted by defects. No band assignments have been given for this material in the literature.

Two films identified as VO_2 by Raman microscopy were further investigated by Rutherford backscattering. The results are consistent with the formation of VO_2 films with peaks that can readily be modelled to a 1 : 2 V to O stoichiometry.

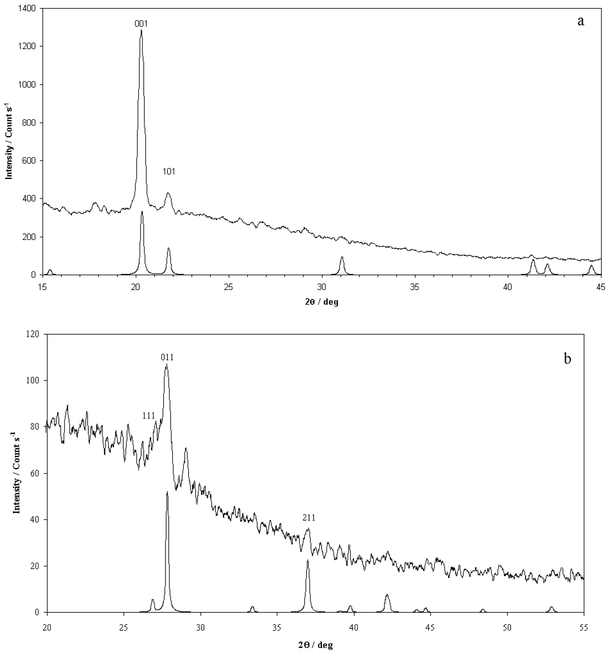

Fig. 3 Experimental and predicted X-ray powder diffraction pattern for a) V_2O_5 film formed by reaction of VCl_4 and H_2O (1 : 10 ratio) at 450 °C; b) VO_2 film formed by reaction of VCl_4 and H_2O (1 : 7 ratio) at 550 °C.

Glancing angle X-ray diffraction patterns showed that various phases were deposited in the APCVD process dependent on the reaction conditions, and included monoclinic VO_2 and V_2O_5 phases (Fig. 3). In one instance a film identified as VO_2(B) the metastable form of the oxide was identified, but this could not be repeated. The phases observed from the X-ray analysis correlated exactly with the conclusions drawn on the basis of the Raman measurements. Some preferred orientation in the (011) direction was observed for the monoclinic VO_2 samples, this led to insufficient peaks for an accurate indexing. Comparison with literature spectra[2] enabled the assignment of Miller indexes. No unambiguous XRD pattern could be obtained for the V_6O_{13} and VO_x films, presumably as they were too thin. The films of V_2O_5 could be indexed to an orthorhombic cell with parameters a = 11.598, b = 4.371, c = 3.413 Å. It was noted that, if the deposition was conducted on glass without a barrier coating, some sodium could be leached from the glass and formed sodium vanadium oxide films.

SEM showed uniformly thick surfaces for all the vanadium oxide series of coatings. This was consistent with an island growth mechanism. EDX measurements showed only the expected amount of vanadium and oxygen in the films with undetectable chlorine contamination (less than 1 atom%).

Functional analysis

Contact angle measurements showed that all of the vanadium oxide films formed by APCVD were hydrophobic with contact angles in the range 40–60°. The SiO_2 coated glass used in this study had a contact angle of 70°. The different phases of vanadium oxides did not show any photocatalytic response to an overlayer of stearic acid, except for the monoclinic VO_2 films; these showed a 50% destruction of an overlayer of a test organic material—stearic acid—after irradiation with 254 nm radiation for 2 h. The uncoated glass and the other vanadium oxide phases showed a negligible loss of stearic acid under the same conditions (*ca.* 1–2% loss).

Thin films of TiO_2 in both the rutile and anatase forms show low contact angle measurements (5–20°) and marked photocatalytic destruction of an overlayer of stearic acid.[17] The monoclinic VO_2 films have the same stoichiometry and

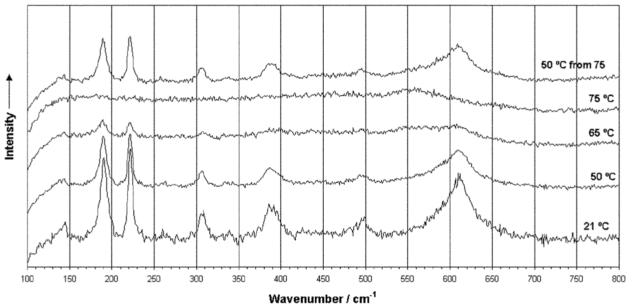

Fig. 4 Raman spectra of a VO_2 film on SiO_2-precoated glass at 21–75 °C (λ_0 = 632.8 nm, power = 2 mW).

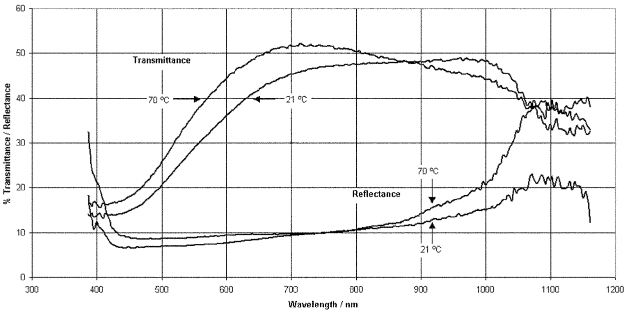

Fig. 5 Reflectance and transmittance spectra of a VO_2 film at 21 °C and 70 °C.

structure as the rutile form of titania. They do show somewhat similar self-cleaning properties as titania coatings (slightly reduced contact angle and some photocatalysis). Presumably this is due to the fact that the vanadium–vanadium contacts are such that electrons are localised in bonding and not available in a conduction band where they might have promoted recombinational processes.

The vanadium dioxide films do show marked thermochromic behaviour that could find usage in intelligent windows. The Raman spectra of VO_2 films at room temperature and at 50, 65, 75 and then 50 °C are shown in Fig. 4. The room temperature and 50 °C spectra are that of monoclinic VO_2, the 65 °C spectrum, a temperature just below the switching temperature, shows all the bands to be greatly reduced in intensity. At 75 °C, which is above the switching temperature, all the low temperature bands have gone and a new band at 555 cm^{-1} is observed; this is the most intense Raman band of tetragonal VO_2. On cooling back to 50 °C the spectrum of monoclinic VO_2 is again obtained, illustrating the reversibility of the transition.

The same transition was also studied optically using reflectance/transmittance measurements. The reflectance and transmittance spectra for a VO_2 film measured at room temperature and 70 °C are shown in Fig. 5. At room temperature the film transmits across most of the visible and IR regions. It also shows low reflectance in the range 400–1150 nm. At 70 °C the transmittance of the film in the 1000–1150 nm region has decreased slightly and, most markedly, the reflectance in this region has increased from 20 to nearly 40%. Repeated cooling and heating cycles showed that the transformation is fully reversible. The changes in reflectance and transmission are associated with the structural change from monoclinic to tetragonal.

Conclusion

APCVD reaction of VCl_4 and water yields thin films of a range of vanadium oxides, VO_2, VO_x, V_6O_{13} and V_2O_5 on glass substrates. Higher deposition temperatures encourage the formation of phases *e.g.* VO_2 which are less rich in oxygen. On the other hand, higher concentrations of vanadium tetrachloride in the gas phase promote the formation of oxygen rich films such as V_6O_{13}. The VO_2 films formed in this study show reversible switching behaviour at 68 °C corresponding to a monoclinic-to-tetragonal phase transition. Surprisingly they also show limited self-cleaning properties such as significant photocatalytic activity to an overlayer of stearic acid.

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References

1 F. J. Morin, *Phys. Rev. Lett.*, 1959, **3**, 34.
2 A. Magneli and G. Andersson, *Acta. Chem. Scand.*, 1995, **9**, 1378; K. D. Rogers, *Powder Diffr.*, 1993, **8**, 240.
3 F. Beteile and J. Livage, *J. Sol–Gel Sci. Technol.*, 1998, **13**, 915; C. G. Granqvist, *Thin Solid Films*, 1990, **193**, 730.
4 M. H. Lee, M. G. Kim and H. K. Song, *Thin Solid Films*, 1996, **291**, 30.
5 J. Livage, *Coord. Chem. Rev.*, 1999, **192**, 391; C. B. Greenberg, *Thin Solid Films*, 1983, **110**, 73.
6 T. Maruyama and Y. Ikuta, *J. Mater. Sci.*, 1993, **28**, 5073.
7 D. Barreca, L. E. Depero, E. Franzato, G. A. Rizzi, L. Sangaletti, E. Tondello and U. Vettori, *J. Electrochem. Soc.*, 1999, **146**, 551.
8 M. N. Field and I. P. Parkin, *J. Mater. Chem.*, 2000, **10**, 1863.
9 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, pp. 1144–46.
10 F. Theobold, R. Cabala and J. Bernard, *J. Solid State Chem.*, 1976, **17**, 431.
11 J. C. Parker, *Phys. Rev. B*, 1990, **42**, 3164.
12 A. G. Aronov, D. N. Mirlin, I. I. Reshina and F. A. Chudrovski, *Fiz. Tverd. Tela (Leningrad)*, 1977, **19**, 193; A. G. Aronov, D. N. Mirlin, I. I. Reshina and F. A. Chudrovski, *Sov. Phys. Solid State (Engl. Transl.)*, 1977, **19**, 110.
13 M. Benmoussa, E. Ibnouelghazi, A. Bennouna and E. L. Ameziane, *Thin Solid Films*, 1995, **265**, 22; I. Kosacki, M. Massot, M. Balkanski and H. L. Tuller, *Mater. Sci. Eng., B*, 1992, **12**, 345.
14 G. Gorenstein, A. Khelfa, J. P. Guesdon, G. A. Narzi, O. M. Hussain, I. Ivanov and C. Julien, *Solid State Ionics*, 1995, **76**, 133.
15 C. Julien, G. A. Narzi and O. Bergstrom, *Phys. Status Solidi B*, 1997, **201**, 319.
16 J. Wang, H. D. Li, Y. J. Fei, X. Wang, Y. Y. Xiong, Y. X. Nie and K. A. Feng, *Appl. Surf. Sci.*, 2001, **177**, 8.
17 S. Sitkiewitz and A. Heller, *New J. Chem.*, 1996, **20**, 233.