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Electrical and optical properties of metal-insulator-transition VO_2 thin films

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Abstract Vanadium dioxide thin films were deposited using *in situ* pulsed laser deposition technique on *a*-, *c*-, and *r*-plane Al_2O_3, and MgO(100) substrates. Microstructure of the films was varied between epitaxial VO_2, polycrystalline VO_2, mixtures of VO_2 and V_6O_{13} with VO_2 as the main phase, and mixtures of VO_2 and V_6O_{13} with V_6O_{13} as the main phase by controlling the deposition oxygen partial pressure. Detailed XRD, SPM, and FESEM measurements were performed in order to analyze the structure of the films. Resistivity as a function of temperature, current–voltage characteristics in electric current induced Joule heating transition process, and the optical transmittance both in insulator and metal states were measured. MIT effect led to 10^3–10^5 change in resistivity with varying transition temperature and hysteresis loop widths. The largest and the steepest transitions were found in the films with polycrystalline microstructure deposited at higher oxygen pressures. Epitaxial films had 2.5 times higher insulator state conductivity than polycrystalline films, which lead to a clearly smaller switching powers in MIT effect generated by Joule heating. However, the optical properties in both states were not considerable affected by conductivity or microstructure properties. The relationships between the microstructure, electrical and optical properties, as well as MIT switching effect together its dynamics in the films are discussed.

Keywords VO_2 · Metal-insulator-transition · Conductivity mechanisms · Optical properties

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1 Introduction

Swift development in optical communications, measurement, and, for example, in camera technology has made demands on the performance of optical fibers, photonics, and optical signal processing components. In order to fulfill these requirements of increasing speed and data processing capability, integrated solid state photonics components, such as waveguides, phase shifters, and modulators, shutters, and sensors, that maintain processing of data in optical form are needed [1, 2]. These devices do not only require development of properties of conventional optical materials, but also introduction of new functionality and new materials into the field. One attractive candidate is metal-insulator transition (MIT) ceramics vanadium dioxide, VO_2. Metal-insulator transition of VO_2 takes place at around 68°C. At this temperature vanadium dioxide undergoes phase transformation from low-temperature monoclinic phase to high-temperature tetragonal phase. During this transformation from insulator to metal, the conductivity of VO_2 increases abruptly. The change of conductivity can be as large as six orders of magnitude in the case of bulk single crystals and around five orders of magnitude in the case of thin films deposited on single crystal substrates [3]. During the transition, also the optical properties of vanadium dioxide are changed, especially at the near-infrared wavelengths, where the optical transmission decreases abruptly close to zero when phase transformation from insulator to metal occurs [4]. This property makes VO_2 thin films suitable for a large variety of optical applications.

In this paper we examine the switching properties of VO_2 thin films during the conventional and electric-current induced Joule heating processes. Especially, the relationship between films microstructure, determined by the

deposition process, and conduction mechanism are studied, and their effect on switching properties and optical response are considered. Also, the dependence of MIT switching dynamics and response time on electrical properties of the films are calculated and shortly discussed.

2 Experimental

Vanadium dioxide thin films were deposited using XeCl excimer laser operating at 308nm wavelength and pulse duration of 25ns. Pulse repetition rate used in film deposition was 5Hz. Films were deposited by using pure ceramic V_2O_5 target. Laser pulse energy density was adjusted to be at the surface of the target 3J/cm^2. Films were deposited on four different types of substrates. These substrates were *a*-, *c*-, and *r*-plane sapphire (Al_2O_3) and magnesium oxide (MgO(100)). The distance between target and the substrate was 3.25cm. The vacuum chamber was first evacuated to a base pressure of 10^{-5}mbar. The oxygen background pressure of the chamber was varied between 6.0×10^{-3} and 1.8×10^{-2}mbar. Temperature of the substrate during the deposition was 400°C. Optical transmission spectra of the VO_2 thin films were measured by using Varian Carry 500 UV–Vis–NIR spectrophotometer. Two measurements were conducted to each sample. First the wavelength was swept from 300 to 2100 nm at the room temperature and the optical transmission data was recorded. After this the sample was heated above the metal-insulator transition temperature to approximately 80°C and the wavelength sweep was repeated. Electrical switching properties of the vanadium dioxide films were studied by using a probe station and computer controlled Keithley 2612 SYSTEM Sourcemeter. Before the measurement, an array of platinum measurement pads with varying geometries was prepared on the surface of the thin film samples by using standard lithographic process and rf-sputtering. The measurement pad array contained six pairs of pads with widths of 50, 130, 180, 200, 300, and 500 μm. The silt between the pads varied from 3 to 6μm. Measurement was carried out by placing the probe needles of the probe station on the measurement pads of the sample, and sweeping the voltage from zero to positive and negative maxim and back across the transition voltage. The changes of current were recorded to study the hysteresis related to the metal-insulator transition of the VO_2. Serial resistor R_s = 500 Ω was added to the circuit to limit the current of the metallic state.

3 Results and discussion

Metal-insulator transition properties of VO_2 thin films were measured using three different kinds of measurement techniques. First, the resistance of certain thin-film configuration was measured as a function of temperature and the change of resistivity through MIT was calculated. Secondly, current-voltage characteristics were measured and the Joule heating generated MIT and corresponding switching power were recorded. Finally, optical transmittance of VO_2 films at UV–Vis–NIR wavelengths of both insulating and metal state was measured and, after simulations and fitting, optical material parameters were obtained.

In Fig. 1, there are shown four resistivity curves of VO_2 thin-films with different crystal structures deposited on *r*- and *a*-plane Al_2O_3 substrates and in various oxygen partial pressures. Crystal structure characterization data of these films has been published previously [5]. In the case of VO_2 film deposited on *a*-plane sapphire in the oxygen partial pressure $p(O_2) = 1.3 \times 10^{-2}$mbar, the ratio of room temperature resistivity ρ_{RT} and resistivity at 90°C ρ_{90C} was 8.9×10^3 and the width of the hysteresis loop ΔT_{MIT} was 2.5°C. This was the best result obtained from the samples deposited on *a*-, *c*-plane Al_2O_3, and MgO substrates, and is actually an implication of the minimization of epitaxial misfit strain in this system. The result was also supported by the fact that the transition temperature was the lowest for films on *a*-plane Al_2O_3, around 64–66°C, whereas the temperature was found to be ten degrees higher for films on *c*-plane Al_2O_3. On the other hand, the films deposited on *r*-plane sapphire had a clear dependence of their electrical properties on the deposition oxygen pressure. When the deposition oxygen pressure was increased, the films were first epitaxial at 0.6×10^{-2}mbar, and typically had XRD reflections from two separate crystal planes at 1.0×10^{-2}mbar. At the pressure of 1.3×10^{-2}mbar, the films were polycrystalline and the thickest of them included also minor V_6O_{13} phase, and finally at the pressure of 1.8×10^{-2}mbar, films were found to be mainly

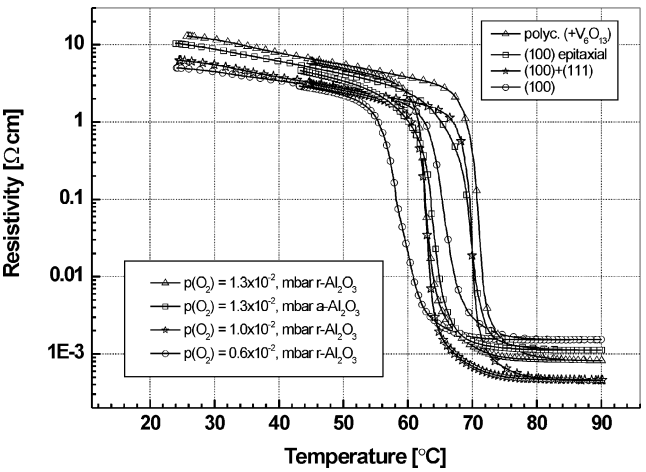

Fig. 1 Resistivity as a function of temperature of four different VO_2 thin films having different microstructures deposited on *a*- and *r*-plane Al_2O_3 substrates at various oxygen partial pressures

in V_6O_{13} phase. As shown in Fig. 1, the best transition properties were achieved again in the films deposited at $p(O_2)$ = 1.3 × 10^{-2}mbar on *r*-plane sapphire having ρ_{RT}/ρ_{90C} = 1.5 × 10^4 and ΔT_{MIT} = 7.3°C.

Current–voltage characteristics of a VO_2 film with the thickness of 163nm and the surface electrodes 180μm in width is shown in Fig. 2. First, the source voltage was increased from zero to 32V, when Joule heating induced MIT occurs, and the current flowing in the circuit increased abruptly to the value limited by the series resistor R_s. After this, VO_2 stays in metal state as long as the current density is high enough, and finally returns to semiconducting state when the source voltage is decreased back to value of 3V. Similar results have been reported by several groups [6, 7]. Same data are shown in Fig. 3, now only calculated into the form of current density *J* flowing through VO_2 film when electric field *E* was applied over it. Another *J*–*E* curve is presented in Fig. 4 showing a switching loop of a sample with similar electrode structure. Now, the switching electric field is much smaller, but the current density higher, than in the case shown in Fig. 3. The values of transition point current densities *J* as a function of applied electric field *E* of larger group of samples are collected into the graph shown in Fig. 5. The dependence of the transition behavior on the deposition oxygen pressure $p(O_2)$ is clearly seen so that the films deposited at 0.6 × 10^{-2}mbar have a *J*–*E* curve like in Fig. 4 with small switching field *E* and higher current density *J*, and when $p(O_2)$ increases, the *J*–*E* characteristics gradually changes into the form shown in Fig. 3 with high *E* and smaller *J*. This effect is believed to origin from the differences in the insulating state conductivities of VO_2 films deposited at different $p(O_2)$ atmospheres. Actually, high $p(O_2)$ was found to lead to polycrystalline VO_2 films with blocking grain boundaries and decreased conductivity in comparison to films deposited at $p(O_2)$ = 0.6 × 10^{-2}mbar,

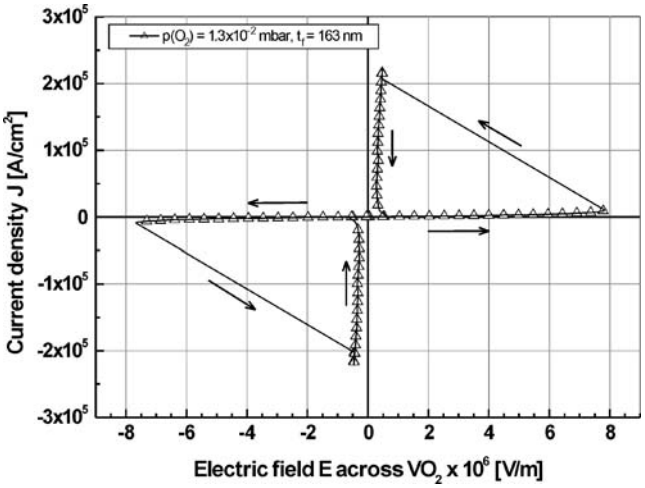

Fig. 3 The data presented in Fig. 2 now normalised to current density *J* − electric field *E* characteristics of the VO_2 thin-film sample geometry

which were always epitaxial, most likely with quite stoichiometric crystal structure, and 2.5 times higher conductivity, as is shown in Fig. 6. Using the resistivity data measured at the temperatures from room temperature up to 60°C in insulating state, or to be more precise in this context, in semiconducting state of the films, the activation energy of $E_a \approx 0.12$ eV could be calculated for thermally activated *n*-type conduction of electrons. Using the electron density $n \approx 1 \times 10^{21}$cm^{-3} reported in literature for monoclinic VO_2 [8], the mobility value of μ = 4.4 × 10^{-4}cm^2/Vs was calculated. According to the Drude model [9], the rate at which heat *Q* is generated per unit volume, and which eventually leads to the increase of the temperature, d*Q* / d*t*, is related to electric power $P_V \propto JE = \sigma E^2$, and hence the increased insulator state conductivity σ is believed to have an important contribution to change in switching behavior shown in Figs. 3 and 4. Especially,

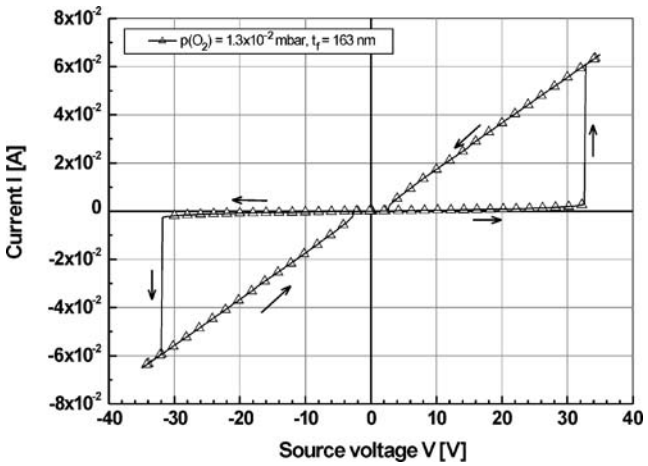

Fig. 2 Current–voltage characteristics of the test circuit with a VO_2 film with the thickness of 163 nm deposited at the pressure of $p(O_2)$= 1.3×10^{-2} mbar in series with resistor R_s=500 Ω

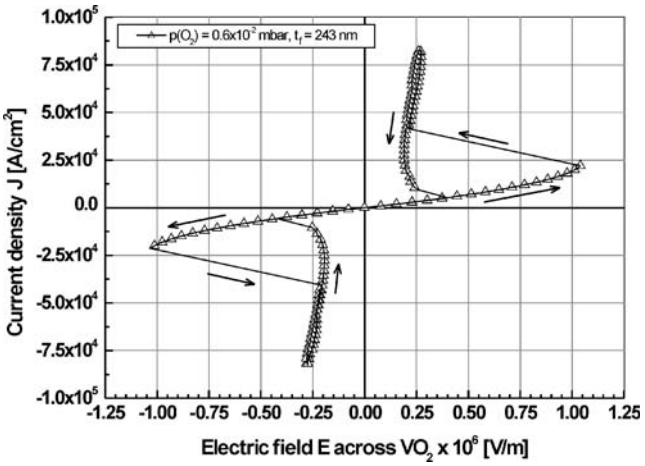

Fig. 4 Current density *J* − electric field *E* characteristics of the VO_2 thin-film sample with thickness of 243 nm and deposited at the pressure of $p(O_2)$=0.6×10^{-2} mbar

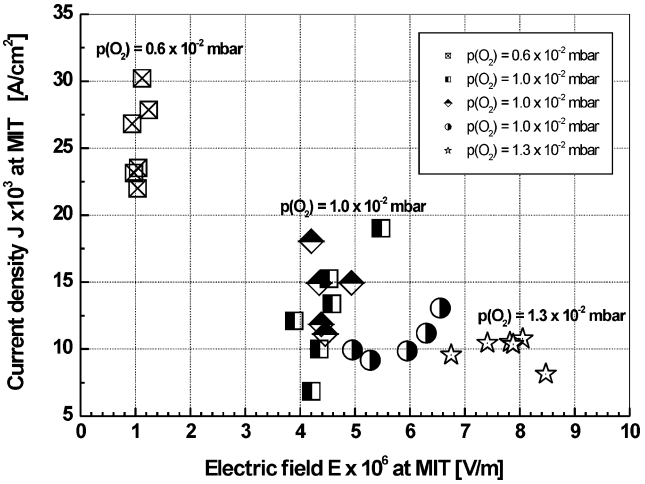

Fig. 5 Graph of MIT switching current density J as a function of corresponding switching electric field E applied over the VO_2 film in the case of electric current induced Joule heating process from insulating to metal state in first quarter of J–E graph

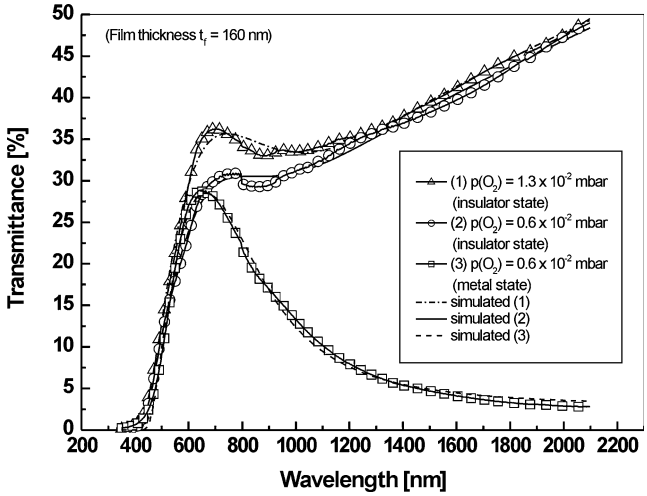

Fig. 7 Measured and fitted optical transmittance of VO_2 films with the thickness of 160 nm and deposited at $p(O_2)=1.3\times10^{-2}$ mbar and $p(O_2)=0.6\times10^{-2}$ mbar at the UV–Vis–NIR wavelengths. From latter, both insulator and metal state transmittances are shown

when switching power per unit volume values P_V were compared between epitaxial and polycrystalline films, the ratio ~0.39 was obtained, in good agreement with the inverse ratio of conductivities and data presented in Fig. 5, respectively.

Power consumption and component dynamics are important factors when MIT switching effect by Joule heating process is considered. If one assumes that the heat conduction of substrate is the only loss of energy in the process, the heat transfer equation at transition temperature T_{MIT} can be simplified in the form:

$$\int_0^t \left[I^2(t)R - \kappa A \frac{\mathrm{d}T}{\mathrm{d}x} \right] \mathrm{d}t = mc[T_{MIT} - T_0], \qquad (1)$$

where $I(t)$ is heating current, R is resistance of VO_2 thin film sample, κ is thermal conductivity of substrate, A is area against substrate, $\mathrm{d}T/\mathrm{d}x$ is temperature gradient across substrate, m is the mass, c is heat capacity of VO_2, and T_0 is the component temperature at the time when heating current is turned on (room temperature in these calculations). The model seems to be actually quite reasonable since the heat source, the film itself with thickness of $t_f <$ 200 nm, and the electrodes with thickness of $t_f \approx 100$ nm, are very thin in comparison to dimensions forming the area $A >$ 50 × 4 μm, and, in addition, since the increase of temperature required for transition $\Delta T \approx T_{MT} - T_o \approx 45°C$ is also very small. Radiation loss and heat conduction through electrodes are insignificant in such a case [10]. MIT effect and component geometry determined transition time τ can now be roughly estimated by using the model presented in Eq. 1, and by assuming that a time-constant electric field E, corresponding the transition field E_{MIT}, switched on in a step-function like manner at the time $t = 0$, is applied over VO_2 film. The generated heat, $P\tau$, should

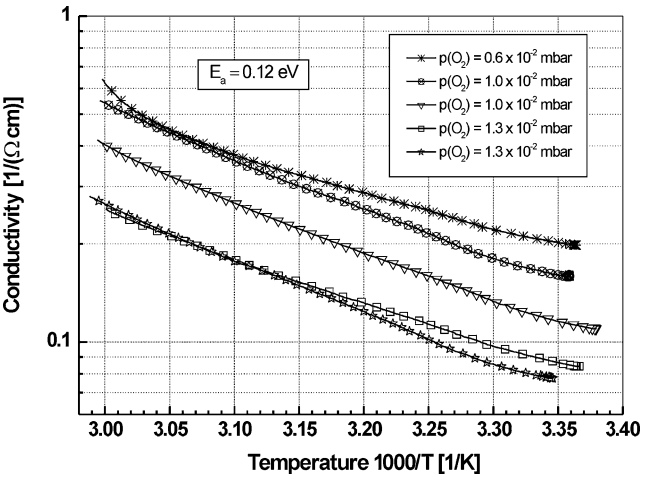

Fig. 6 Conductivity as a function temperature of VO_2 films deposited on r-plane Al_2O_3 substrates at various oxygen partial pressures

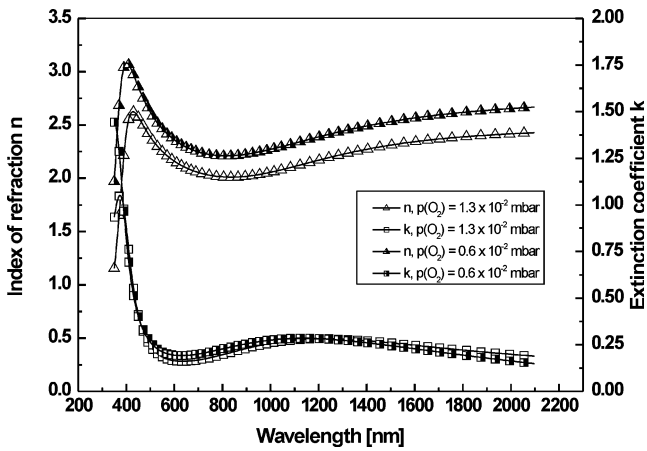

Fig. 8 Calculated values of refractive index n and extinction coefficient k based on fitting of data shown in Fig. 7

correspond to the sum of transition heat and substrate heat-conduction losses, $\sim P_s\tau$, and thus Eq. 1 can be modified in to form:

$$\tau \approx \frac{mc\Delta T}{(P - P_s)}. \quad (2)$$

Since the measured *J–E* characteristics were found to be essentially independent of scanning rate in the measurements where voltage was increased in steps of 200mV after every 0.25, 0.5, or 1.0s, the calculated transition power values at $dV / dt = 0.4$ V/s could be considered as steady state values. Using measured transition power value P = 143.6mW and known bulk material parameters for the epitaxial film deposited at $p(O_2) = 0.6 \times 10^{-2}$mbar, having area A = 500μm × 4.7μm and thickness of 245nm, a transition time $\tau = 2.25 \times 10^{-7}$ s could be calculated. This is in good agreement with the results presented by Chae et al. when component mass is scaled, since the switching field and current density are comparable [11].

In Fig. 7, there are three transmittance $T(\lambda)$ curves measured from VO_2 thin films with the thickness of 160nm at UV–Vis–NIR wavelengths. Insulator state $T(\lambda)$ is pretty much the same at longer wavelengths for both samples, only there is 5% higher transmittance below 1200nm in the polycrystalline film deposited at higher oxygen pressure. In the metal state, the transmittance curves are almost identical. Insulator state $T(\lambda)$ data was reasonably fitted with Lorentz multiple oscillator model with RMSE < 0.5, and the calculated values of refractive index n and extinction coefficient k as a function of wavelength are presented in Fig. 8. Since the extinction coefficients are essentially the same for both cases, the differences in $T(\lambda)$ can be attributed to variation in the surface morphology so that the epitaxial film deposited at $p(O_2) = 0.6 \times 10^{-2}$mbar had flatter surface, rms roughness $R_q \approx 4.0$ nm, actually, and thus higher reflectance at shorter wavelengths.

4 Conclusions

Vanadium dioxide VO_2 thin films were deposited by *in situ* pulsed laser deposition on *a*-, *c*-, and *r*-plane sapphire (Al_2O_3) and magnesium oxide (MgO(100)) substrates at various oxygen partial pressures between 0.6×10^{-2} and 1.8×10^{-2}mbar. The microstructure and crystal orientation of the films could be controlled from epitaxial highly oriented pure VO_2 films to polycrystalline VO_2, and further to films also containing minor phase of V_6O_{13}. Crystal structure determined the MIT switching properties of the films so that epitaxial films has transitions greatly dependent on the epitaxial misfit strain, where as the polycrystalline films had the strongest MIT effects with multiplication up to 1.5×10^4. On the other hand, the epitaxial films had higher conductivities that made them easier to be switched into metal state by using the Joule heating process. Optical properties were found to be essentially independent on the microstructure and transition properties, especially at IR wavelengths.

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References

1. Z. Liu, P.-T. Lin, B.W. Wessels, F. Yi, S.-T. Ho, Appl. Phys. Lett. **90**, 201104 (2007)
2. J. Hiltunen, D. Seneviratne, R. Sun, M. Stolfi, H.L. Tuller, J. Lappalainen, V. Lantto, Appl. Phys. Lett. **89**, 242904 (2006)
3. Z.P. Wu, S. Yamamoto, A. Miyashita, Z.J. Zhang, K. Narumi, H. Naramoto, J. Phys. Condens. Matter. **10**, L765–L771 (1998)
4. N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Groult, J. Appl. Electrochem. **28**, 41–48 (1998)
5. J. Lappalainen, S. Heinilehto, S. Saukko, V. Lantto, H. Jantunen, Sensor. Actuat. A-Phys., in press, (2007) DOI 10.1016/j.sna.2007.05.002
6. H.-T. Kim, B.-G. Chae, D.-H. Youn, G. Kim, K.-Y. Kang, S.-J. Lee, K. Kim, Y.-S. Lim, Appl. Phys. Lett. **86**, 242101 (2005)
7. C.-R. Cho, S. Cho, S. Vadim, R. Jung, I. Yoo, Thin Solid Films **495**, 375–379 (2006)
8. B. Felde, W. Niessner, D. Schalch, A. Scharman, M. Werling, Thin Solid Films **305**, 61–65 (1997)
9. C.M. Wolfe, N. Holonyak Jr., G.E. Stillman, *Physical Properties of Semiconductors* (Prentice-Hall, New Jersey, 1989), p. 160
10. N.A. Kuldin, A.A. Velichko, A.L. Pergament, G.B. Stefanovich, P.P. Boriskov, Tech. Phys. Lett. **31**, 520–523 (2005)
11. B.-G. Chae, H.-T. Kim, D.-H. Youn, K.-Y. Kang, Physica B **369**, 76–80 (2005)