Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 3760–3764
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Characterisation and ac-electrical investigation of sublimated bis(dimethylglyoximato)palladium(II) thin films

A.A. Dakhel [a,*], Ahmed Y. Ali-Mohamed [b]

[a] Department of Physics, College of Science, University of Bahrain, P.O. Box 32038, Bahrain
[b] Department of Chemistry, College of Science, University of Bahrain, P.O. Box 32038, Bahrain

Received 25 March 2006; received in revised form 11 May 2006; accepted 12 May 2006
Available online 27 May 2006

Abstract

Thin films of bis(dimethylglyoximato)palladium(II) complex of polycrystalline structure were prepared by sublimation in a vacuum at 140 °C, on glass and p-Si substrates. The films were characterised by spectral optical absorption, energy dispersion X-ray fluorescence (EDXRF), and X-ray diffraction (XRD) methods. After characterisation, metal–insulator (complex)–semiconductor MIS devices were fabricated to measure the frequency dependence of ac-conductivity in a range of 5–100 kHz. Data of ac-measurements follow the correlated barrier-hopping CBH model, from which one of the fundamental absorption peaks, the minimum hopping distance, and other parameters of the CBH model were determined, connecting and relating the optical, structural, and electrical measurements. The dielectric properties of the complex were studied through Debye model, from which the relaxation time for the dipoles (2.45×10^{-6} s) and the molecular dipole moment (3.63×10^{-30} C m) were determined.

Keywords: Insulating films; Bis(dimethylglyoximato)palladium(II); Dielectric phenomena; CBH model

1. Introduction

The studies of electrical, structural and optical properties of metal-substituted organic complexes (MSO), based on different metallic ions, have attracted much attention due to their possible applications in electronic and optoelectronic devices. Among MSO are the bis(dimethylglyoximato) of d^8 transition metals (II) like Ni, Pt, or Pd of identical planar molecular configuration discussed in Ref. [1,2]. The strong covalent bonds between metal ions and ligand in bis(dimethylglyoximato)metal enhance the stability of the molecules [1] that permits the sublimation in some temperature range without thermal decomposition. In crystalline state, the dioxime planar molecules of d^8 transition metals stack face-to-face, forming a one-dimensional columnar structure in *c*-direction, in which the central metal ions of adjacent molecules separated by about 0.325 nm [1–3] interact strongly with each other forming a linear metal chain [2–4]. This interaction provides electronic delocalisation that is responsible for many remarkable physical, electronic and optical properties [3,5–7], like strong optical absorption in the visible region [8,9].

The aim of the present investigation is to study the optical, structural and ac-electrical properties of the vacuum-deposited bis(dimethylglyoximato)palladium(II) [$Pd(dmgH)_2$] thin films. For optical study, films were deposited on glass substrate and for electrical study, samples were fabricated in form of metal–$Pd(dmg)_2$–Si MIS structure.

2. Experimental details

The bis(dimethylglyoximato)palladium(II) compound was prepared from a solution that contains not more than 0.1 g of Pd: [$Pd(NO_3)_2 \cdot 2H_2O$,GPR,BDH] in 250 mL of 0.25 M with respect to nitric acid (Puriss, Fluka Chemica) and a 1% solution of dimethylglyoxime in 95% ethyl alcohol (Puriss, Fluka Chemica) was added. The detailed

* Corresponding author.
E-mail address: adakhil@sci.uob.bh (A.A. Dakhel).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.05.028

procedure of the synthesis is discussed in Ref. [10]. The orange-yellow precipitate of bis(dimethylglyoximato)palladium(II) was washed with cold deionised water and then with not deionised water and dried at 110 °C to constant weight. It was weighted as $[Pd(C_4H_7O_2N_2)_2]$.

Thin film samples were slowly deposited (0.1 nm/s) by thermal sublimation at about 140 °C in a vacuum system of about 10^{-3} Pa on Si and glass substrates held at room temperature. Thermal sublimation must take place in a temperature interval of 100–160 °C in order to avoid thermal decomposition [11]. The p-Si wafer substrates were thermo-chemically cleaned with 50% potassium hydroxide. The samples were post-annealed at 90 °C for 30 min. For construction of metal–insulator–semiconductor MIS structure for electrical investigation, aluminum films of about 150 nm were deposited to form gate of area 4π mm^2 and back contacts. The samples thickness was monitored by a thickness monitor and then measured by Gaertner 117 ellipsometer of $\lambda = 632.8$ nm to be 183.7 nm.

The Pd composition of the film samples and the constituent powder were probed by energy dispersion X-ray fluorescence (EDXRF) method with Ni-filtered Cu Kα radiation and Amptek XR-100CR, X-ray detector of energy resolution 180 eV at 5.9 keV. The crystal structure was investigated by a Philips PW 1729 X-ray diffractometer with Cu Kα radiation. The electrical measurements were done with a Keithley 614 electrometer and a Keithley 3330 LCZ instrument of a signal 50 mV.

3. Characterisation of the prepared thin film sample

Fig. 1 shows the EDXRF spectrum of $Pd(dmg)_2$ powder and thin film grown on Si substrate. As seen, Pd L band signal of energy range 2.84–3.17 eV radiated from thin film sample appears with a Si Kα signal of energy 1.74 keV from the substrate (the energies of signals in Fig. 1 were determined by the spectrum of pure elements and using Bearden X-ray tables [12]). The appearance of the Pd signal from the prepared thin film demonstrates the stability of $Pd(dmgH)_2$ molecules during the vacuum sublimation at about 140 °C.

The X-ray diffraction (XRD) pattern of thin film and powder of $Pd(dmg)_2$ are depicted in Fig. 2. The powder diffraction, which was analysed with Crystal-Cracker (build 186) X-ray program [13] shows that the crystal structure is orthorhombic of *Ibam* space group of $a = 1.676$ nm, $b = 1.049$ nm, and $c = 0.650$ nm, as information given in Ref. [14]. However, there were some reflections (3 0 2 and 1 1 3) identified from orthorhombic structure of primitive space group rather than *Ibam*. The XRD pattern of thin film shows the appearance of only *Ibam* reflections, indicating a unified space group film, which was nearly textured in [1 1 0] direction. The average grain size (gs), as defined in Ref. [15] was calculated from the most intense (2 2 0) peak to be about 48.9 nm. The annealing of the film at 70 °C for 30 min did not introduce changes in the structure or gs of the as-prepared film.

The prepared films were characterised by a spectral optical absorption method. The normal spectral absorbance $A(\lambda)$ of films grown on glass substrates in the transparent and absorption region (200–1100 nm) are shown in Fig. 3. Two films were optically studied, the as-deposited film and the post-annealed film at 70 °C for 30 min. The absorbance data were corrected relative to the optically identical uncoated glass substrate. All the investigated samples have high transparency $T > 0.90$ in the transparent region. The absorption spectrum of the post-annealed film shows more absorption features than that of the as-prepared film. Generally, the absorption peaks in the visible region, at 465 nm for the as-deposited film and at (465 nm and 425 nm) for annealed film arise from d → d transitions in Pd ions. The appearance of these two energy bands is due to the splitting of the 4d-band of Pd(II) under

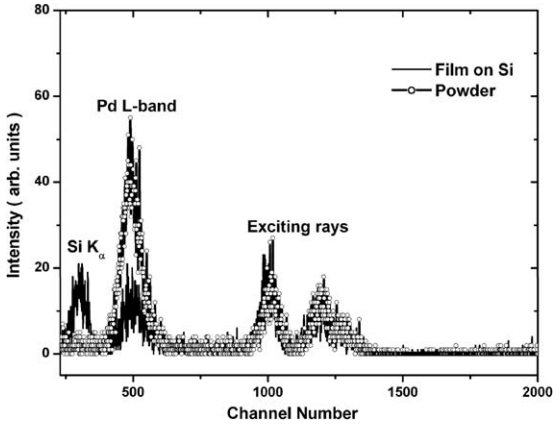

Fig. 1. XRF spectrum of bis(dimethylglyoximato)palladium(II) powder and thin film grown on Si substrate. The exciting line was Ni-filtered Cu Kα line.

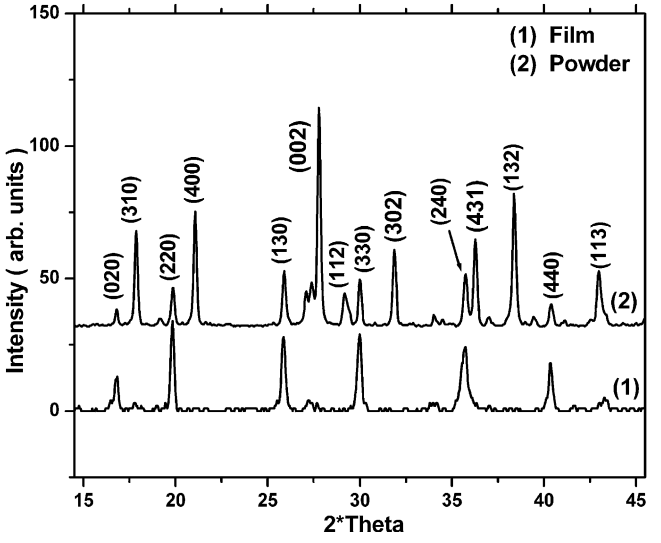

Fig. 2. X-ray diffraction of bis(dimethylglyoximato)palladium(II) powder and film. The X-ray beam was Ni-filtered Cu Kα and the scan speed was 0.01 °/s.

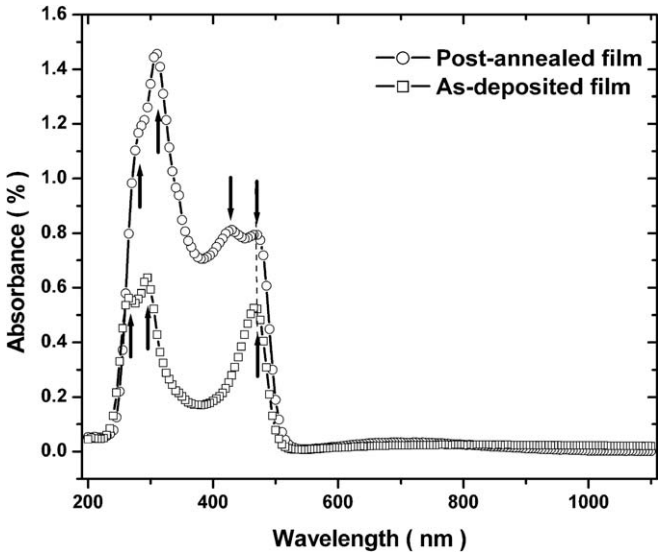

Fig. 3. The spectral absorbance of the prepared bis(dimethylglyoximato)palladium(II) thin film grown on glass substrate. Squares refer to as-deposited film of absorption peaks at (465 nm, 295 nm, and 265 nm) and circles refer to the annealed (at 70 °C for 30 min) film of absorption peaks at (465 nm, 425 nm, 310 nm, and 280 nm).

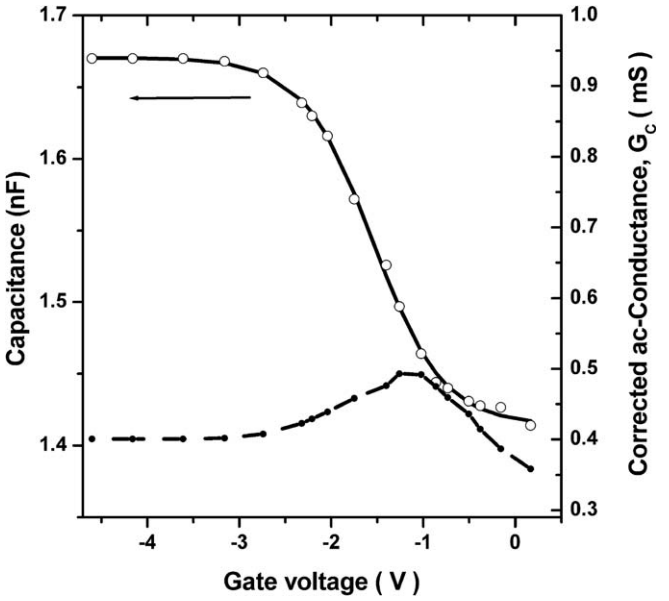

Fig. 4. The gate–voltage dependence of the capacitance and corrected conductance of bis(dimethylglyoximato) palladium(II) film as insulator of MIS device measured at 1 MHz.

the influence of the intermolecular field [1]. The absorption peaks in UV region at (295 nm and 265 nm) for the as-deposited film and at (310 nm and 280 nm) for the annealed film are more intense than the visible peaks, assigned as metal-to-ligand charge transfer (CT) band [16], and its energy location is more sensitive to the field surrounding the $Pd(dmg)_2$ molecule than the visible band. The difference between the spectra of the two films reflects the changes in the stoichiometry and crystal-structural relaxation due to the usual annealing effects, which influence the inter- and intra-molecular interaction field. Such effects can influence on the 4d-band splitting energy distribution.

The constructed metal–insulator-Si MIS structure used for electrical measurements was characterised by a standard known method of measuring the capacitance and conductance as a function of gate voltage at 1 MHz [17,18] as shown in Fig. 4, which shows the capacitance–gate voltage (C–V_g) and the corrected conductance–gate voltage (G_c–V_g) dependence carried on the sample. The correction of the parallel conductance (G_c) for the series resistance was done according to the theoretical relations given in Ref. [19] applied for a certain (1 MHz) frequency. From data of Fig. 4 it was estimated the fixed charge density (Q_{ins}) of about 1.1×10^{11} cm^{-2} and the interface trap density (D_{it}) of about 1.8×10^{12} eV^{-1}/cm^2.

The capacitance and dielectric loss measurements of MIS device in accumulation state that is controlled by the dielectric properties of the bulk insulator [17,18] are used to calculate the dielectric properties of the insulator like the real part ε' and the imaginary part ε'' of the relative permittivity (RP) in addition to the electrical conductivity σ_{ac}.

4. Electrical measurements

The ac-conductivity of insulators can be expressed as a sum of two contributions [20], $\sigma_{ac}=\sigma_{dc}(0)+\sigma_{ac}(\omega)$, where $\sigma_{dc}(0)$ is the dc-conductivity and $\sigma_{ac}(\omega)$ is the frequency-dependent part of the conductivity, which usually expressed in a power dependent [21,22],

$$\sigma_{ac}(\omega)=A_\sigma\omega^s \quad (1)$$

where A_σ is the pre-exponential and the exponent s is of value $s\leqslant 1$ depending on the insulating film microstructure. This power law is essentially due to the hopping of charge carriers [20], which based its universality. The appropriate theoretical model that describe the conductivity $\sigma_{ac}(\omega)$ is the correlated barrier hopping (CBH) model, according to which the pre-exponential A_σ is given by [23,24] $A_\sigma=C(\alpha N_{LS})^2/\tau_0^\beta\varepsilon_{ins}^5W_M^6$, where $C=e_6/24\pi^3\varepsilon_0^5=0.415\times10^{-60}$ C V^5 m^5, W_M is the maximum barrier height for hopping in eV, N_{LS} is the trap (or localised states) concentration in m^{-3}, $\alpha=n_{el}^{7/2}$, n_{el} is the number of simultaneously hopped electrons between centres, τ_o is the effective relaxation time (approximately 10^{-13} s), and $\beta=1-s$. The exponent s is given at operating temperature T for randomly distributed hopping centres by: $s=1-6\,k_BT[W_M+k_BT\ln(\omega\tau_o)]^{-1}$.

Fig. 5 shows the room-temperature frequency dependence of the ac-conductivity σ_{ac} in a frequency range of 5–100 kHz. We mention here that, for lower frequencies a larger influence of the interfacial charges on the electrical measurements would defect the results [25]. The analysis shows that the CBH model is convenient to explain the experimental data and the fitting value of s was 0.96, which corresponds to $W_M\approx4.2$ eV. This value is equal to the

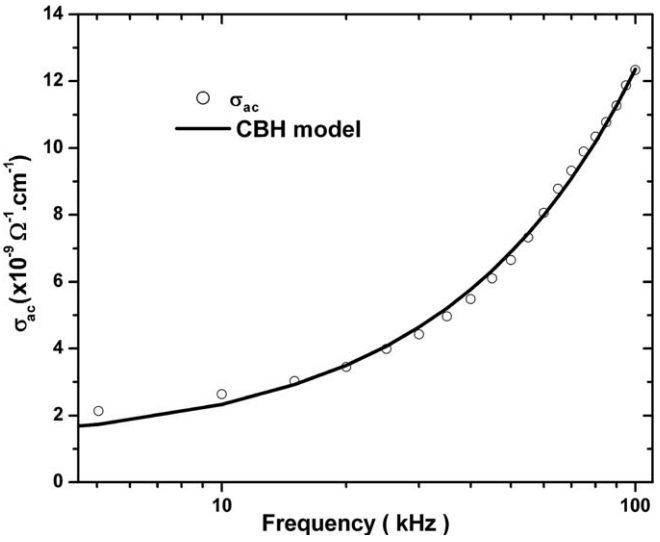

Fig. 5. Frequency dependence of the ac conductivity σ_{ac} measured at room temperature under accumulation gate voltage (−3.0 V) for polycrystalline $Pd(dmg)_2$ film grown on Si substrate.

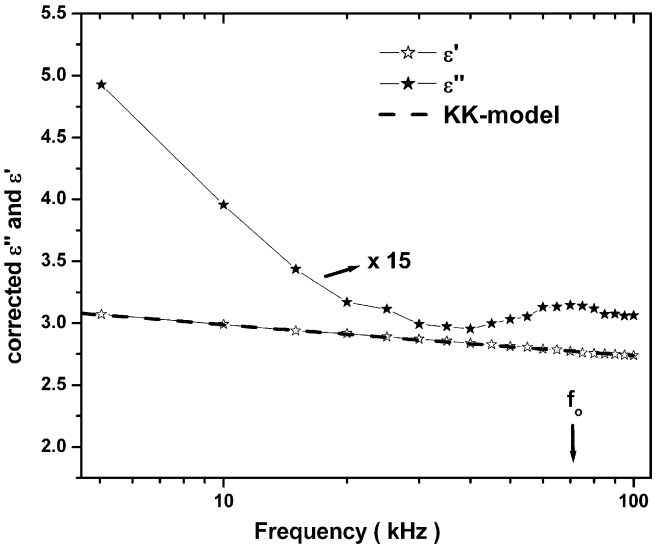

Fig. 6. Variation of real part ε' and corrected imaginary ε'' part of the relative permittivity measured at room temperature under accumulation gate voltage (−3.0 V) for polycrystalline $Pd(dmg)_2$ film grown on Si substrate.

energy of one of the absorption peaks (at 295 nm for as-deposited and 310 nm for annealed film), as seen in Fig. 3. According to the original CBH theory [23], the value of W_M is equal to the energy of the absorption edge for bipolaron conduction. This result should not be applied in the present case as long as we deal with molecular crystals of complicated structure, which cannot be considered having electronic or mobility energy spectrum of same nature as that of normal atomic insulator: valence and conduction band. However, the fitting of the experimental data to CBH model yields the value of density of localised states or hopping centres (αN_{LS}) of 1.4×10^{21} cm^{-3}, which is comparable to the concentration of Pd ions (3.47×10^{21} cm^{-3}) calculated from bulk data. This means that the conduction is realised by mono-polaron hopping process ($\alpha = 1$). The minimum (cutoff) hopping jump (R_{min}) [26] was calculated to be about 0.5 nm (which is close to the ion–ion separation in the linear metal chain 0.325 nm), which must equal to the effective intermolecular separation, as stated by Bruetting et al. [27]. In addition, the application of the power law gives the value of σ_{dc} (1.1×10^{-9} S/cm), which is almost identical with that value measured directly by dc technique.

Real and imaginary parts of RP: the real part of the relative permittivity (RP) ε' calculated from the capacitance measurement at accumulation gate voltage of −3 V, is slowly decreasing function of frequency, $\varepsilon' \sim f^{-0.04}$ and getting the value 2.75 at 100 kHz, as shown in Fig. 6. This variation is consistent with the Kramers–Kronig (KK) relations that the power-law following of the ac-conductivity of an insulator causes the RP to follow the relation [28]:$\varepsilon' \propto \omega^{s'-1}$, where $s' = s$ in the present case. The small values of ε' suggest to use the bis(dimethylglyoximato)palladium(II) as low-k material in construction of microelectronic devices.

The measured imaginary part of RP was corrected due to the transfer of electrical charges from one electrode to the other. The correction is related to dc-conductivity (or $\sigma_{dc}/\varepsilon_o\omega$) and the corrected ε'' can be obtained using the following equation [29]:

$$\varepsilon''(\omega) = (\sigma_{ac} - \sigma_{dc})/\varepsilon_0\omega \quad (2)$$

Therefore, the dielectric loss ε'' in Eq. (2) computes the contribution from dipoles, defects, and localised or bound charges. The frequency dependence of ε'' is depicted in Fig. 6, where one can observe a resonance peak at about $f_0 = 65$ kHz corresponding to a relaxation time τ of about 2.45×10^{-6} s. Such dependence $\varepsilon''(\omega)$ is appropriate to the polarisation resonance associated with the lattice vibrations. Then, it is possible to calculate the molecular dipole moment p by applying the well-known Debye equation for ε'' [30,31]:

$$\varepsilon'' = \frac{A/T}{1 + \omega^2\tau^2}\omega\tau \quad (3)$$

where T is the operating temperature in K. The dipole strength A is given by: $A = Np^2/3\varepsilon_0 k_B$, where N is the dipole concentration (3.47×10^{21} cm^{-3}), k_B is the Boltzmann constant, and ε_0 is the permittivity of free space. The fitting of the $\varepsilon''(\omega)$ data around the peak to Eq. (3) gives $A = 124.5$ K at 293 K and $p = 3.63 \times 10^{-30}$ C m, which has an ordinary order on magnitude. Fig. 7 shows the Cole–Cole plot of ε'' against ε' for data points around the resonance peak f_0. According to Debye theory, the Cole–Cole plot is a semicircle with centre at $(1/2(\varepsilon_s + \varepsilon_\infty), 0)$ and of radius $1/2(\varepsilon_s - \varepsilon_\infty)$, where ε_s and ε_∞ are the low- and high-frequency limits, respectively, of the real part of the RP [30]. The calculation gives 2.98 and 2.56 for ε_s

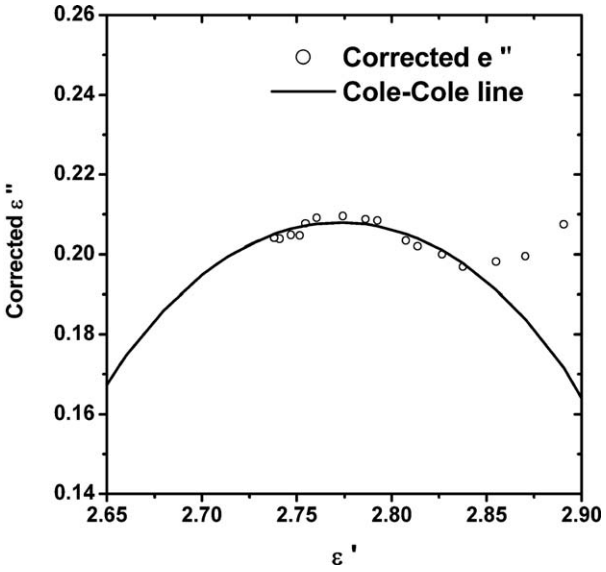

Fig. 7. The Cole–Cole plot of ε'' versus ε' for $Pd(dmg)_2$ film grown on Si substrate.

and ε_∞, respectively. These values are consistent with those obtained from Fig. 6, where $(\varepsilon_s - \varepsilon_\infty) = A/T$.

5. Conclusions

It was found that the prepared $Pd(dmg)_2$ polycrystalline film by sublimation method has an orthorhombic structure of *Ibam* space group. The ac behaviour of the prepared film shows that it follows the power-law and CBH model for conduction by a single polaron hopping inter-molecules. The concentration of hopping centres ($1.4 \times 10^{21}\,cm^{-3}$) and the effective intermolecular separation (0.5 nm) were determined from the application of a CBH model. The obtained RP is very slowly dependent on the frequency and getting only 2.75 at 100 kHz. The small values of ε' suggest to use the bis(dimethylglyoximato)palladium(II) as low-k material in construction of microelectronic devices. The dielectric properties of the complex were studies through Debye model, from which the relaxation time for the dipoles (2.45×10^{-6} s) and the molecular dipole moment (3.63×10^{-30} C m) were determined.

References

[1] J.C. Bailar, Jr., H.J. Emeleus, R. Nyholm, A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon press, Oxford, 1975.
[2] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Butterworth-Heinemann, Oxford, 2001, pp. 1152–1160.
[3] K. Yamamoto, T. Kamata, Y. Yoshida, K. Yase, F. Mizukami, T. Ohta, Adv. Mater. 10 (1999) 1018.
[4] H. Endres, H.J. Keller, R. Lehmann, A. Proveda, H.H. Rupp, H. van de Sand, Z. Naturforsch. 32b (1977) 516.
[5] M.M. Belombe, J. Solid State Chem. 22 (1977) 151.
[6] M. Tkacz, H.G. Drickamer, J. Chem. Phys. 85 (1986) 1184.
[7] I. Shirotani, A. Kawamura, K. Suzuki, W. Utsumi, T. Yagi, Bull. Chem. Soc. Jpn. 64 (1991) 1607.
[8] J.C. Zahner, H.G. Drickamer, J. Chem. Phys. 33 (1960) 1625.
[9] Y. Ohashi, I. Hanazaki, S. Nagakura, Inorg. Chem. 9 (1970) 2551.
[10] A.I. Vogal, A Text-book of Quantitative Inorganic Analysis Including Elementary Instrument Analysis, third ed., Longman, London, 1972, pp. 511–512.
[11] V. Cominos, A. Gavriilidis, Eur. Phys. J. AP 15 (2001) 23.
[12] J.A. Bearden, X-Ray Wavelengths, Rev. Mod. Phys. (January) (1967) 86–99.
[13] Kurt Leinenweber, Crystal-Cracker (build 186) X-ray program. Available from: <http://multianvil.asu.edu/Crystal_Cracker>.
[14] M. Sakhawat Hussain, B.E.V. Salinas, E.O. Schlemper, Acta Crystallogr. B 45 (1979) 628.
[15] E.F. Kaelble (Ed.), Handbook of X-rays for Diffraction, Emission, Absorption, and Microscopy, McGraw-Hill, New York, 1967, p. 17-5.
[16] J.E. Caton, C.V. Banks, Talanta 13 (1966) 967.
[17] S.M. Sze, Physics of Semiconductor Devices, second ed., John Wiley & Sons Inc, 1981.
[18] W.H. Hill, Solid State Electron. 23 (1980) 987.
[19] S. Pal, D.N. Bose, Appl. Surf. Sci. 181 (2001) 179.
[20] R.M. Hill, A.K. Jonscher, J. Non-Cryst. Solids 32 (1979) 53.
[21] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, second ed., Clarendon Press, Oxford, 1979.
[22] R.H. Chen, R.Y. Chang, S.C. Shern, J. Phys. Chem. Solids 63 (2002) 2069.
[23] S.R. Elliott, Adv. Phys. 36 (1987) 135.
[24] S.R. Elliott, Phil. Mag. 36 (1977) 1291.
[25] E.H. Nicollian, A. Goetzberger, Bell Syst. Tech. J. 46 (1967) 1055.
[26] R. Salam, Phys. Stat. Sol. (a) 117 (1990) 535.
[27] W. Bruetting, S. Berleb, A.G. Mueckl, Synthetic Metals 122 (2001) 99.
[28] A. Ghosh, Phys. Rev. B 41 (1990) 1479.
[29] H.B. Lal, J. Phys. C: Solid St. Phys. 13 (1980) 3969.
[30] J. McConnell, Rotational Brownian Motion and Dielectric Theory, Oxford, London, 1980, p. 31.
[31] N.E. Hill, W.E. Vaughan, A.H. Price, M. Davies, Dielectric Properties and Molecular Behaviour, Van Nostrand Reinhold Co. Ltd., London, 1969.