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

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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

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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

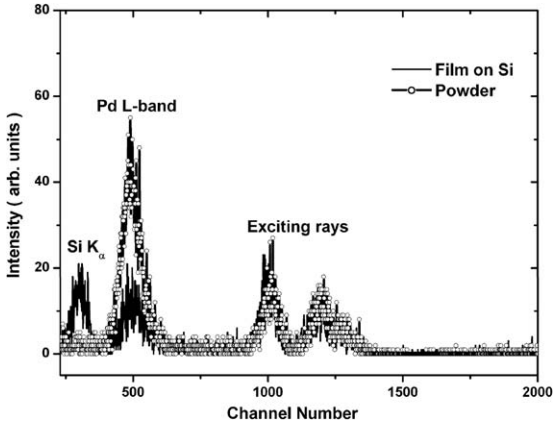

Fig. 1. XRF spectrum of bis(dimethylglyoximato)palladium(II) powder and thin film grown on Si substrate. The exciting line was Ni-filtered Cu Kα line.

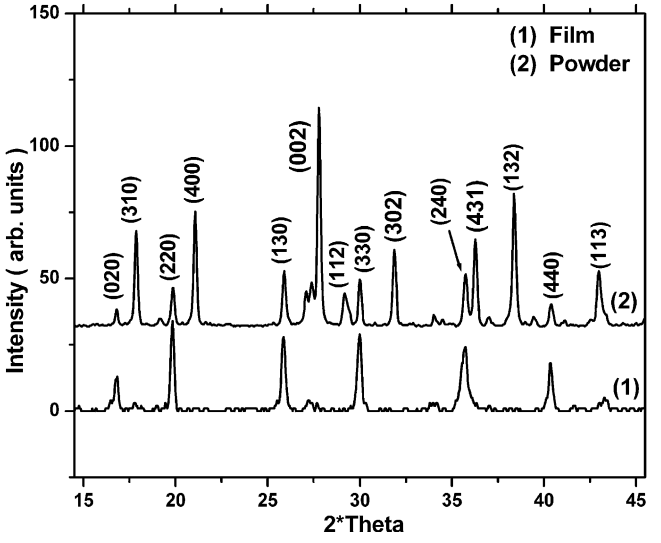

Fig. 2. X-ray diffraction of bis(dimethylglyoximato)palladium(II) powder and film. The X-ray beam was Ni-filtered Cu Kα and the scan speed was 0.01 °/s.