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Single crystal ruthenium(II) complex dye based photodiode

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ABSTRACT

The electrical and photoresponse properties of Ruthenium(II) complex dye based on photodiode were analyzed by current, capacitance and conductance measurements performed in a wide illumination intensity and frequency range. It was observed that the reverse current increases with increasing illumination intensity. The results confirm that the photodiode exhibits a photoconducting behavior. Also, the transient photocurrent, photocapacitance and photoconductance of the photodiode were investigated as a function of time. It was observed that the values of these parameters increase after illuminating and reach back to original value after turning off the illumination. In addition, the interface states and series resistance of the photodiode were determined from capacitance/conductance–voltage measurements. The value of these parameters decreases with increasing frequency. The obtained experimental results suggest that the photodiode with Ruthenium/Ru(II) complex thin film could be used in various optoelectronic devices and applications.

1. Introduction

The electrochemical, optical and electrical properties of transition metal complexes have made them invaluable for optoelectronic and electronic devices. The transition metals such as ruthenium(Ru), rhodium(Rh), iridium(Ir) and osmium(Os) are metals with high tensile strength and good conductor of heat and electricity. Ru(II) complexes are a transition-metal complexes and are molecules with photoactivation as well as their usage in catalysis [1–4]. On the other hand, Ru(II) complexes containing ligands such as pyridine-based tridentate triamine and bidentate diamine compounds have unique photochemical and photophysical properties.

Photodiodes which are sensitive to high-energy particles and photons are the most versatile semiconductor optoelectronic devices. They transform light into current and are designed to operate in reverse bias. Also, a photodiode is a photodetector which has one of the structures among p-n, p-i-n, or Schottky junction where photo-generated carriers are swept by the built-in electric field [5–10]. When the photodiode is illuminated by light of energy greater than the semiconductor bandgap energy, photo-generated electron–hole pairs electron–hole pairs occur. If these pairs are created within the space charge region, the electric field in the junction separates the charges and drifts them to the neutral regions. In other words, the separated electrons and holes must diffuse in different directions to avoid electron–hole recombination. The carrier drift generates a photocurrent in the external circuit that provide an electrical signal. The photoresponse effect in the reverse bias region is considerable higher than the forward bias region and the variation of photocurrent with light intensity was investigated in the reverse bias.

In this study, the electrical and photoresponse properties of Au/Ru(II) complex/n-Si photodiode were investigated. The photovoltaic characteristics of the photodiode were studied by the illumination-dependent current–voltage measurements. Moreover, the frequency dependence of electrical characteristics of the

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photodiode were investigated by using capacitance/conductance–voltage measurements.

2. Experimental details

2.1. Crystal structure determination

Ru(II) complex was synthesized according to the literature [2]. Single crystal for X-ray diffraction measurement was obtained by slow evaporation of Ru(II) complex solution in DMF. Data collection was performed on a STOE IPDS II diffractometer at room temperature (296 K) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA [11] while data reduction was applied using X-RED32 [11]. The structure was solved by direct methods using SHELXS-2013 [12] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2014 [13] implemented in WinGX [14] program suit. All of the C-bound H atoms were inserted in idealized positions and treated using a riding model, fixing the bond lengths at 0.93 and 0.96 Å for CH and CH_3 atoms, respectively. The displacement parameters of the H atoms were fixed at $U_{iso}(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of their parent atoms. The crystal contains channel voids filled with disordered water molecules along the c-axis. Therefore, hydrogen atoms of the solvent water molecules could not located but are included in the formula. Further details of the structural analysis are given in Table 1. The general-purpose crystallographic tool PLATON [15] was used for the structure analysis and presentation of the results. Molecular graphic was generated by using DIAMOND [16].

2.2. Preparation of the photodiode

Ruthenium(II) complex solution was deposited on n-Si substrate by using spin-coating technique. Before deposition of the Ru(II) complex, the native oxide layer of the silicon substrate was etched by HF and then rinsed in deionized water using an ultrasonic bath for 10–15 min. Finally, the silicon wafer was chemically cleaned according to method based on successive baths of methanol and acetone. To prepare the photodiode, firstly, an ohmic contact was prepared on back side of n-Si substrates by evaporating of Al metal. The solution of Ru(II) complex was prepared in dimethylformamide (DMF) and it was drop casted on the surface of the silicon wafer and dried at 50 °C for 10 min. Then, it was cooled to room temperature. Top contact of the photodiode was prepared by Au metal. For this, Au metal was evaporated by sputtering system in the form of circles giving a photodiode contact area of 7.85×10^{-3} cm^2. The obtained diode structure is Au/Ru(II) complex/n-Si. The current–voltage (I–V) measurements of the photodiode were performed with KEITHLEY 4200 semiconductor characterization system. Photoresponse measurements were performed using a solar simulator. The intensity of the illumination was measured using a solar power meter (TM-206). The capacitance/conductance–voltage (C/G–V) measurements were performed with Keithley 4200 semiconductor characterization system.

3. Results and discussion

3.1. Structure description of Ru(II) complex

In this work, a Ru(II) complex containing a tridentate triamine and a bidentate diamine ligands was synthesized according to the literature method [2]. Synthesized schema is depicted in Fig. 1. Solid state structure of Ru(II) complex was determined by single crystal X-ray diffraction technique. A DIAMOND drawing of the cationic moiety is shown in Fig. 2, while the important bond lengths and angles are collected in Table 2. The asymmetric unit of the compound contains a discrete complex cation, one chloride counter anion and two solvent water molecules. The cationic complex is composed of a tridentate (1E,1′E)-1,1'-(pyridine-2,6-diyl)bis(N-phenylethan-1-imine) ligand with a Ru(II) metal center, a bidentate

Table 1
Crystal data and structure refinement parameters for Ru(II) complex.

CCDC deposition no.	1451191
Color/shape	Black/prism
Chemical formula	$[RuCl(C_{21}H_{19}N_3)(C_{12}H_{12}N_2)]^+ \cdot Cl^- \cdot 2(H_2O)$
Formula weight	705.63
Temperature (K)	296
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	C2/c (No. 15)
Unit cell parameters	
a, b, c (Å)	34.1306(13), 25.6734(10), 9.4333(3)
α, β, γ (°)	90, 97.581(3), 90
Volume (Å^3)	8193.7(5)
Z	8
D_{calc} (g/cm^3)	1.144
μ (mm^{-1})	0.543
Absorption correction	Integration
T_{min}, T_{max}	0.8238, 0.9618
F_{000}	2896
Crystal size (mm^3)	0.46 × 0.15 × 0.11
Diffractometer/measurement method	STOE IPDS II/rotation (ω scan)
Index ranges	$-41 \le h \le 41$, $-31 \le k \le 31$, $-11 \le l \le 11$
θ range for data collection (°)	$1.97 \le \theta \le 25.67$
Reflections collected	44982
Independent/observed reflections	7733/2111
R_{int}	0.237
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7733/0/392
Goodness-of-fit on F^2	0.819
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0850$, $wR_2 = 0.2044$
R indices (all data)	$R_1 = 0.2569$, $wR_2 = 0.2780$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.60, −0.43