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A novel photodiode based on Ruthenium(II) complex containing polydentate pyridine as photocatalyst

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ABSTRACT

Ruthenium(II)-complex thin film, bearing pyridine-based tridentate was deposited on p-Si substrate by spin coating technique. The I–V measurements across the junction showed rectifying behavior. The reverse bias current of the heterojunction diode increased with increasing illumination intensity. The sensitivity to the light of *I–V* characteristics was attributed to the photocatalytic effect of Ruthenium(II)-complex. Ruthenium(II)-complex thin film exhibited a transparency higher than 70% in the visible part of the spectrum. The band gap of Ruthenium(II)-complex film was calculated to be 4.42 eV. The reflectance data can be analyzed to determine optical constants such as refractive index and dielectric constant. The results indicate that Ruthenium(II)-complex can be used in fabrication of high photosensitive diodes.

1. Introduction

In recent years, the optoelectronic devices based on thin films have received great attention. The photodiode is one of these devices. Much research has been carried out to develop the performance of photodiodes [1–4]. However, in order to maintain a good interface with the silicon substrate for high mobility, many types of organic materials have been used as interfacial layer. Wahab et al. [5] reported that the thin film of cobalt phthalocyanine (CoPc) was effective for control of electronic parameters of Al/n–Si diode. The space charge limited conduction (SCLC) was pointed out as the dominant mechanism. For wide-band UV photodiodes, heterojunction diodes (HJDs) utilizing ZnO thin film have attracted considerable attention due to its various advantage [6–9]. The SiO_2 oxide layer in comparison with the Pt/GaN (MS) Schottky diode provides the excellent performance for high temperature detection [10].

The superior electrical and optical properties of complexes have made them invaluable in electronic applications. Ruthenium(II) complexes are molecules with photoactivation as well as their usage in catalysis [11–14]. Ru(II) complexes are advantageous because of tunable electronic, optical and chemical properties, containing ligands such as pyridine-based tridentate triamine and bidentate diamine compounds. The luminescence could be tuned by crystal waters included in the crystals; for example, $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$, $[Ru–(dbb)_2(CN)_2]\cdot H_2O$, and $[Ru(dbb)_2(CN)_2]$ [15]. Photophysical studies have shown that Ruthenium polypyridyl complexes display strong luminescence and emission due to the prolonged lifetime of the excited state [16,17]. Ruthenium complex dyes were assessed as the light-to-electricity conversion agents of the dye-sensitized solar cells (DSSC) [18]. Solid-state dye-sensitized solar cells based on pyrazole-based ligands as the transition metal complex show a highly efficient power conversion efficiency. Burschka et al. [19] synthesized a tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) complex to be used in DSSCs. Photovoltaic characteristics of DSC based on $[Co(bpy\text{-}pz)_2]^{3+/2+}$ system yielded a power conversion efficiency of over 10% at 100 $mWcm^{-2}$ [20,21]. Ruthenium(II) complexes will fulfill the requirements for photo-sensing applications.

In this study, the complex sample was deposited on the surface of the Si substrate by spin-coating technique. The photovoltaic characteristics of organometal Ru(II)-based heterojunction were studied by the illumination-dependent *I–V* measurements. The band gap of Ru(II) thin film was determined by optical absorption measurement.

2. Experimental details

A member (complex 10) of a series of novel Ru(II) complexes (1–10) synthesized in our previous study is given in Ref. [22]. p-type silicon (the thickness of 300 μm) was provided from commercial suppliers and used without further polishing. Novel Ru(II) complex solution was deposited on the silicon wafer and glass substrate by using spin coating technique. After formation of the film onto silicon, aluminum (Al) top contacts were evaporated on the film surface through molybdenum mask. The diode contact area was determined to be 3.14×10^{-2} cm^2. Thus, Al/Ru(II) complex/p-Si structure was obtained. The film thickness was determined using Park System XEI software by tapping-mode atomic force

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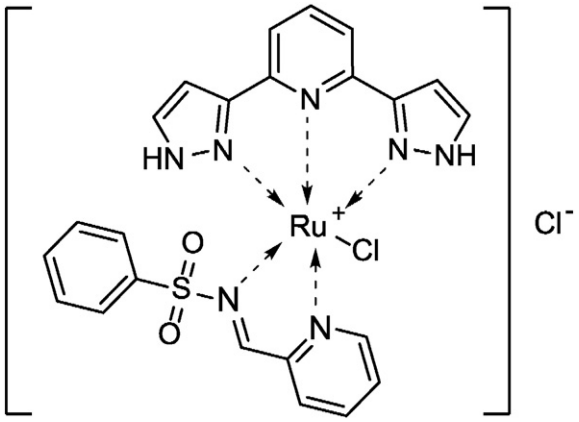

Fig. 1. The molecular structure of the Ru(II) complex in the present work.

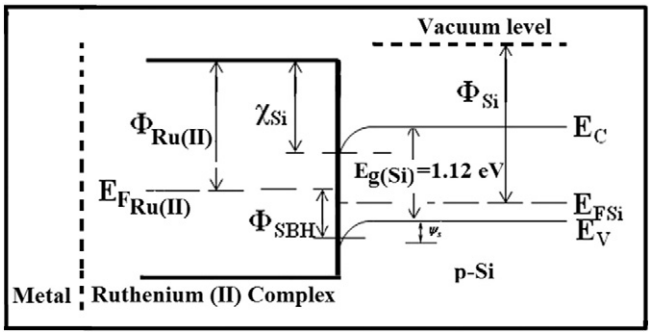

Fig. 3. The energy-band diagram of the Ru(II) complex and Si contact.

microscopy (AFM) and measured to be about 74 ± 1 nm. The current–voltage (I–V) measurements were performed with Keithley's Series 2400 Source Measure Unit (SMU) Instruments. The photoresponse measurements were made using a halogen lamb. The light intensity was monitored by solar powermeter. The optical characterization of the film was done using a Shimadzu UV–VIS–NIR 3600 spectrophotometer.

3. Results and discussion

3.1. The study of morphological and electrical properties

The general formula of the studied Ruthenium(II) complex is [chloro [2,6-di(1*H*-pyrazol-3-yl-κN^2) pyridine-κ*N*] [*N*-[(2-pyridinyl-κ*N*) methylene] [benzene sulfonamide-κ*N*] Ruthenium(II)] chloride. Fig. 1 shows the molecular structure of the Ru(II) complex. Fig. 2 shows AFM images of the complex film (40 × 40 μm^2 and 5 × 5 μm^2 areas). As it is seen in Fig. 2 (second image), the nanoparticles seem to remain embedded in the structure.

Fig. 3 shows the energy band diagram of Al/Ruthenium(II) complex/p-Si structure. Where ψ_s is the surface potential and χ is the electron affinity of Si. Fig. 4 shows the illumination intensity dependence of *I–V* curves for Al/Ruthenium(II) complex/p-Si structure. The heterojunction exhibited a high rectification ratio (RR) of 2.93 × 10^7 at ±2 V and in dark conditions. The rectification ratio was found as a function of illumination intensity. The rectification behavior of Al/Ruthenium(II) complex/p-Si structure decreased from 1.05 × 10^4 to 1.38 × 10^3. However, with the increase of illumination intensity from dark to 5.21 mW/cm^2, the rectification ratio of the ITO/CdS/PANI(polyaniline)/Au heterojunction increased [23]. The PV efficiency and high rectification are attributed to the decreasing thickness of the ferroelectric layer in oxide-based ultra thin p–f–n nano-junctions composed of p-$La_{0.8}Sr_{0.2}MnO_3$ and f-$PbZr_{0.2}Ti_{0.8}O_3$ [24]. Photodiodes are modeled to be sensitive to light. The ratio of current density at light conditions (J_{photo}) is considered as the greater absolute current. The technical meaning of photosensitivity is as follows [25]:

$$P_{R_{I/d}} = \frac{J_{photo}}{J_{dark}}. \quad (1)$$

The photosensitivity value of the Al/Ruthenium(II) complex/p-Si structure was found to be 2.08. The some electrical parameters of Al/Ruthenium(II) complex/p-Si photodiode were tested using the well-known thermionic emission equations in our previous study [26]. The barrier height and ideality factor were found to be 0.90 eV and 1.37, respectively. Ideality factor larger than unity may be ascribed to the existence of complex thin film layer.

The variation of photocurrent vs. illumination intensity for Al/Ruthenium(II) complex/p-Si photodiode is given in Fig. 5. It is seen that the photocurrent of Al/Ruthenium(II) complex/p-Si diode increases with increasing illumination intensity. The photocurrent is expressed as follows [27]:

$$I_{ph} = BP^{\gamma} \quad (2)$$

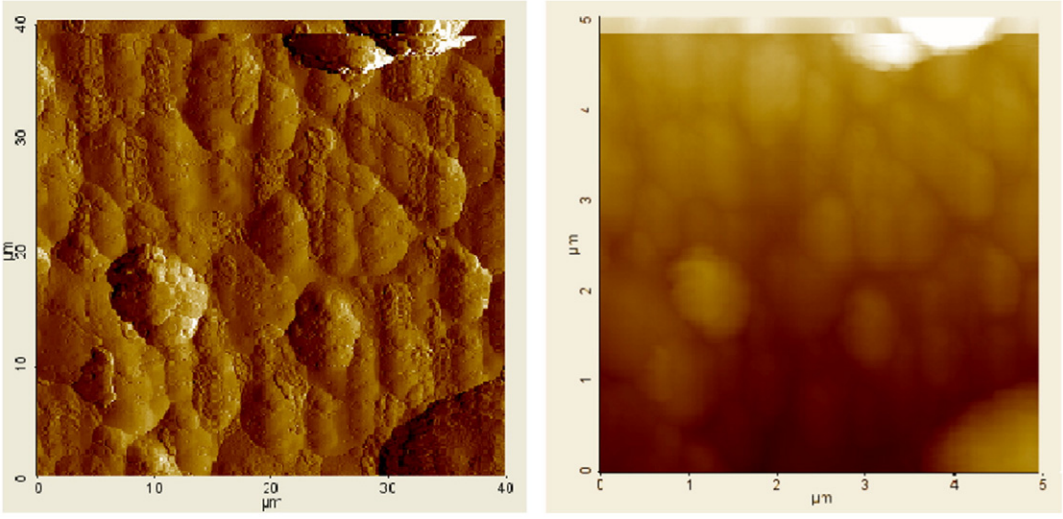

Fig. 2. AFM images of the complex film (40 × 40 μm^2 and 5 × 5 μm^2 areas).