Polypyrrole Electrodeposition on Inorganic Semiconductors $CuInSe_2$ and $CuInS_2$ for Photovoltaic Applications

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Summary: Thin polypyrrole (PPy) layers with an average thickness of about 0.5 μm were deposited, using potentiostatic and galvanostatic techniques, on $CuInSe_2$ (CISe) structures prepared electrochemically on glass/ITO substrates and on $CuInS_2$ (CIS) structures fabricated on Cu tape substrates. The polymer layer of p-type is considered as an alternative to the traditional buffer layer and window layer in the conventional cell structure. The deposition proceeded from an aqueous solution containing sodium naphthalene-2-sulfonate as a dopant. In order to prepare stable PPy films of high quality with a good adherence to the surface of inorganic semiconductors CIS and CISe, the optimal concentrations of reagents, current densities and electrodepositing potentials were selected experimentally. Electrochemical polymerization of pyrrole to PPy on CIS surfaces is faster under white light irradiation and the polymerisation starts at lower potential than in the dark. Significant photovoltage and photocurrent of the fabricated CISe/PPy and CIS/PPy structures have been observed under standard white light illumination.

Keywords: CIS; conducting polymers; electrodeposition; photovoltaic structure; polypyrroles

Introduction

At present, the potentials of photoenergy conversion using electrically conducting polymers (ECP) are under serious investigation due to producing low-cost, large-area and flexible photodiodes and solar cells.[1,2] Although a number of ECP were synthesized, the polypyrrole (PPy) was one of the most intensively studied polymers during the last decade.[3] PPy shows several application advantages like easy synthesis in aqueous media with a wide range of possible dopants, relatively high stability of electric conductivity and good mechanical properties. As noted, the combination of ECP with inorganic semiconductors, e.g. $CuInSe_2$

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(CISe) and $CuInS_2$ (CIS), is attractive for use in thin-film photovoltaic cell structures.[4] CIS and CISe are polycrystalline semiconductors with very high optical absorption coefficients, presently intensively studied for photovoltaic applications.[5,6]

Among various techniques of preparation of these structures with PPy, electrodeposition of the polymer on the surface of CIS and CISe deserves special attention because it can be easily controlled by regulating the polymerization current or potential and time for producing high-quality PPy films with predictable properties.[7] Moreover, electrodeposition is an inexpensive, low-temperature and relatively non-polluting method. However, the process of PPy electrosynthesis on the surface of the semiconductors with high electrical resistance is far from being easily controllable due to non-linear electrical processes in the semiconductors. PPy films with good quality are most often polymerized using certain sulfonic acids and their salts (naphthalenesulfonates, toluenesulfonates, etc.) as dopants with planar aromatic groups. These dopants induce structural regularity in the polymer film. Also, they can absorb more easily on the electrode surface and thus facilitate the first steps of the polymerization, leading to improved adhesion of PPy with high conductivity of the film.[3,7]

PPy always has p-type conductivity when doped with sulfonates, but the type of conductivity in CIS or CISe strongly depends on the composition and defects and may be p- or n-type.[6] The conductivity of n-type in the semiconductors is necessary for the formation of a rectifying heterojunction between PPy and CISe layers. The purpose of our work is to determine the optimal conditions of electrochemical preparation of high-quality PPy films with a good adherence to CIS and CISe and to investigate the obtained structures. In order to prepare these photovoltaic structures, the optimal concentrations of reagents, current densities and electrodepositing potentials were selected experimentally.

Experimental

Electrodeposition of n-CISe thin films with the thickness of about 1 μm onto ITO/glass substrates in potentiostatic mode at –900 mV using a Wenking LT 87 potentiostat have been described in a previous paper.[8] Aqueous solutions containing $CuSO_4/In_2(SO_4)_3/SeO_2$ in concentrations of 2/8/11 and 3/7/11 mM, respectively, were used for CISe(2-8-11) and CISe(3-7-11) films deposition. Thermal annealing of as-deposited CISe films was performed at 400 °C for 20 min in vacuum. Subsequently, the CISe films were etched in 10% KCN aqueous solution for 5 min to remove possible secondary phases.

CIS films have been prepared on copper tape substrate using the CISCuT method.[9] The idea

of the method is a fast roll-to-roll sulfurization in S_x+N_2 gas atmosphere at 500-600 °C of 0.8 μm indium precursor on the copper tape substrate. Fast chemical reaction of indium and copper from the substrate with sulfur from the gas phase results in formation of a stack of several layers at the surface. The top layer of the stack has been shown to be a low-doped $CuInS_2$ phase. Prior to PPy deposition, the structure was etched in aqueous KCN solution and annealed in vacuum at 280 °C for 10 min.

Thin doped PPy films were synthesized on the surface of glass/ITO/CISe and Cu/CIS substrates galvanostatically or potentiostatically in the usual three-electrode electrochemical cell configuration using a VoltaLab™ 32 potentiostat/galvanostat in the dark and under white light illumination of 100 mW/cm^2. Pyrrole (Py) monomer (Aldrich) was distilled in vacuum prior to use. Polymerization was performed in the presence of sodium naphthalene-2-sulfonate (NSA) (Aldrich) as a dopant in de-aerated aqueous solutions of Py. The film thickness was controlled by the charge transferred during electrodeposition using the Faraday law.[10] Experimentally determined optimal values for the current density, applied potential and concentration of reagents are presented in Table 1.

Table 1. Optimal parameters for PPy electrodeposition.

Substrate	PPy deposition	Py/NSA mol/l	Current density mA/cm^2	Potential vs SCE mV	PPy film thickness μm	Deposition time s
ITO/CISe	galvanostatical[a)]	0.3/0.1	0.25-0.5	550-700	0.5-2.0	160-1280
Cu/CIS	galvanostatical[a)]	0.025/0.009, 0.05/0.017	0.125-0.25	450-900	0.5-1.0	320-640
Cu/CIS	galvanostatical[b)]	0.3/0.1	1.0-2.0	60-190	0.5-2.0	40-320
Cu/CIS	potentiostatical[b)]	0.3/0.1	0.05-0.3	-200-0	0.25-0.5	400-1600

[a)] In the dark.
[b)] Under white illumination of 100 mW/cm^2.

Thermal annealing of PPy films at 100 °C for 6 h in air has markedly improved its adherence to CIS and CISe. The metal contact (Ag) was evaporated onto the polymer layer for the structures based on CISe. All investigated photovoltaic structures were fabricated in the sandwich configurations glass/ITO/CISe/PPy/Ag and Cu/CIS/PPy/i-ZnO/n-ZnO respectively. The ZnO:Al window layers were DC-sputtered, the i-ZnO layer was deposited in the presence of oxygen. The thickness of the i-ZnO layer was about 100 nm, the overall thickness of the ZnO window layers was about 1 μm.

Current-voltage characteristics were measured using a VoltaLab™ 32 potentiostat/galvanostat

and Keithley 2400 SourceMeter. White light with an intensity of 100 mW/cm^2 from a tungsten-halogen lamp or xenon lamp was used for irradiation. The glass/ITO/CISe/PPy samples were illuminated from the glass substrate side. The area of the CISe/PPy/Ag and CIS/Ppy/ZnO junctions was about 1 and 0.1 cm^2, respectively. In the case of Cu/CIS/PPy, the polymer layer side was illuminated since CIS was deposited on the Cu substrate.

Results and Discussion

It is well known that electrodeposition of PPy is remarkably sensitive to the conditions at the surface of the substrate, e.g., to the adsorption of the monomer or oligomers at the electrode surface, the distribution of nucleation centers and the charge and potential distribution at the electrode/electrolyte interface. Frequently, the nucleation sites are sparsely occupied on the surface, resulting in a semicircular and insular morphology.[7] It has been found that NSA is highly suitable as a dopant for the deposition of smooth and adhesive PPy films onto the CIS and CISe layers. Figure 1 shows the electrode potential vs. time during galvanostatical deposition of PPy onto glass/ITO/CISe and Cu/CIS substrates in the presence of NSA as a dopant in the dark and under white light illumination.

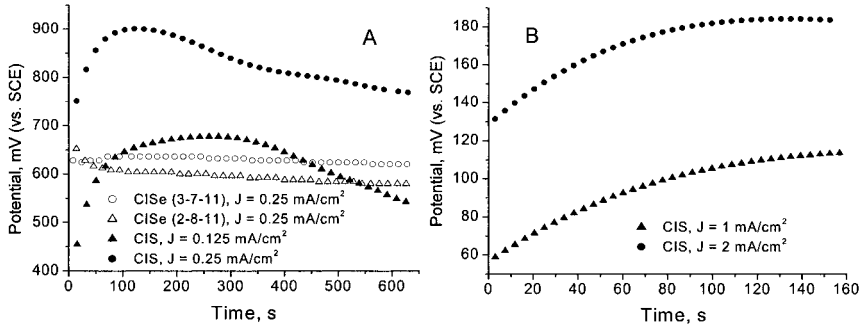

Figure 1. Potential vs SCE during galvanostatic polymerization of Py galvanostatically at glass/ITO/CISe and Cu/CIS substrates: A - in 0.3M Py/0.1M NSA and 0.025M Py/0.009M NSA solutions for the CISe and CIS, respectively, in the dark; B – in 0.3M Py/0.1M NSA solution for the CIS under illumination (100 mW/cm^2).

The influence of illumination on PPy electrodeposition on CIS was investigated by cyclic voltammetry (Figure 2A). The cyclic voltammograms and Figure 1B show the significant role of light in polymerisation of Py on the CIS surface. At lower potentials, the anodic current corresponding to Py oxidative polymerization is substantially larger under illumination than in

the dark. The synthesis of PPy film begins at –200 mV vs. SCE (Figure 2A) and the galvanostatic curves start at low potential when the current density is relatively high: 1 and 2 mA/cm^2 (Figure 1B). The illumination has been found to play two roles during polymerization: (i) primarily it affects the early stages of polymerization by creating high oxidative potential on the CIS surface relative to the substrate due to the so-called "as-grown cell" formed by the CISCuT process and (ii) it seems to enhance the nucleating process of PPy on CIS. These two effects give the possibility to produce high-quality PPy films on the CIS layers at low potentials and to avoid the danger of CIS degradation due to oxidation. Also, relatively high current densities could be achieved. It should be noted that for deposition of PPy films with the thickness less than 0.5 μm the potentiostatic method results in a better lateral homogeneity of the film, in a good agreement with the literary data.[7]

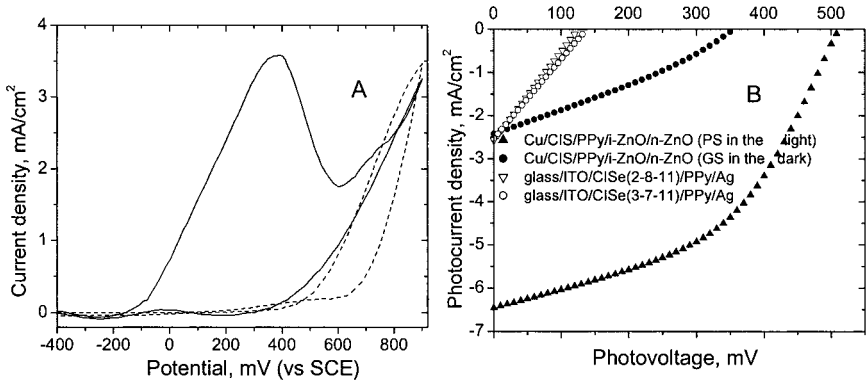

Figure 2. A – Cyclic voltammograms with scan rate of 20 mV/s of PPy doped with NSA deposited on CIS in 0.3M Py/0.1M NSA aqueous solution in the dark and under white light illumination (100 mW/cm^2). B – *I-V* characteristics of the ITO/CISe/PPy/ and Cu/CIS/PPy/i-ZnO/n-ZnO structures under irradiation of 100 mW/cm^2 (GS – PPy layer with the thickness of about 1 μm was deposited galvanostatically at 0.125 mA/cm^2 from 0.025M Py/0.009M NSA aqueous solution in the dark. PS – PPy layer with the thickness of about 0.25 μm was deposited potentiostatically at -200 mV vs. SCE under white light illumination of 100 mW/cm^2). The PPy layers on glass/ITO/CISe substrates were prepared galvanostatically at 0.25 mA/cm^2 in 0.3M Py/0.1M NSA aqueous solution in the dark.

Figure 2B shows photovoltaic properties of the obtained structures under 100 mW/cm^2 white light illumination. The incident light produced a short-circuit photocurrent density I_{sc} = 6.5 mA/cm^2 and an open-circuit voltage V_{oc} = 510 mV for the structure based on the CIS and PPy. The thickness of PPy film has noticeably affected the I_{sc} and V_{oc} because of the light

absorption in PPy. In further studies, thinner CISe and PPy films could be used to improve the parameters of both types of the structures. The linearity of *I-V* characteristics of glass/ITO/CISe/PPy/Ag structures suggests the possibility that the photovoltaic behaviour could be fully controlled by the shunt resistance in the structure. Nevertheless, I_{sc} and V_{oc} are remarkably high and prove the value of the chosen approach.

Conclusions

The optimal conditions for electrodeposition of high-quality PPy films with a good adherence to CIS and CISe were determined in the dark and under illumination. The studies showed that the potentiostatic deposition of thin PPy film onto the CIS under white light illumination is preferable for producing the photovoltaic structures. The best structure so far showed an open circuit voltage of V_{oc} = 510 mV and a short circuit current of I_{sc} = 6.5 mA/cm^2 under xenon lamp white light illumination of 100 mW/cm^2 intensity.

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