



Comparative study of two methods for construction of a composite material consisting of indium microparticles electrodeposited on silicon modified by a Conductive polymer

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ABSTRACT

A new composite material based on the modification of the silicon surface by a polypyrrole film, then the electrodeposition of indium microparticles (Silicon / Polypyrrole-Indium) within the polymeric film has been developed and studied. The deposits are realized electrochemically. The pyrrole polymerization on the surface of silicon was carried out in an organic solution of acetonitrile by cyclic voltammetry. Then indium was deposited by electrochemical reduction in an aqueous solution by two different methods: one by direct reduction in a solution of indium ions and the other by inclusion of ions In^{3+} within the polymeric film. Different conditions that affect the material were studied. The deposits were characterized by electrochemical methods and atomic force microscopy AFM. Electrode materials obtained by the two methods were compared.

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Introduction

One of the most promising technologies of renewable energy is photovoltaic conversion. Photovoltaics (PV) is an efficient way to produce electricity directly from sunlight without care about energy supply or environmental pollution [1,2]. A material composite of different components possesses new properties that none of its constituents possess alone. Silicon is the material most currently used for photovoltaic modules. Indium is a promising candidate for optoelectronic and photovoltaic applications [3]. Particular attention has been paid to organic photovoltaic devices in recent years because of low cost, ease of fabrication, flexibility and manufacture of large area[4].

The semiconductor devices based on heterojunction formed by organic compounds growing on inorganic substrates have been widely studied by many researchers for their potential use in electronic and optoelectronic technologies [5].

Electrochemistry is an important area of research for preparation and development of these materials [6–14].

In this paper, we present our work which consists to develop and characterize a silicon electrode material modified by a

conductive polymer film, and then the microparticles of indium were introduced in the film by two different methods: one by direct reduction in an indium ionic solution and the other one by inclusion of In^{3+} within the polymeric film. We will study the influence of some parameters on the material. We will also compare the electrode materials obtained by the two methods.

Experimental

In our experience, the electrochemical study of indium on silicon has been performed in two different environments. In an aqueous medium, the used solvent is distilled water and the supporting electrolyte is potassium chloride KCl. In an organic medium, the solvent used is acetonitrile, CH_3CN , and the supporting electrolyte is lithium perchlorate, LiClO_4 . The used reagents are indium chloride InCl_3 and the pyrrole monomer. We have used for the characterization of our modified electrode (cyclic voltammetry and coulometry) the VoltaLab 40 (PGZ 301) controlled by a voltmaster software. The experiments were performed in a three electrode cell. The working electrode is a wafer of n-type silicon of orientation (111) and area of 0.30 cm². Before each experiment, the wafers have undergone a chemical pre-treatment. The silicon wafers are cleaned with acetone and ethanol for 10 minutes,

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and then washed thoroughly with distilled water. These plates are then subjected to a chemical treatment with a solution of hydrofluoric acid diluted to 10% for five minutes. The reference electrode has a fixed and constant potential. The auxiliary electrode is a platinum wire.

Results and discussions

Electrodeposition of indium on n-Si (111)

The electrochemical behaviour of indium was studied on an n-silicon electrode of 0.3 cm² surface by digital cyclic voltammetry, in an aqueous solution of indium chloride (InCl₃) 8x10⁻³ M. The voltammogram recorded for one cycle is characterized by the presence of a reduction peak at the vicinity of -1400 mV corresponding to the reduction of the trivalent indium (In⁺⁺⁺) to the metal indium (In⁰), and by the presence of an oxidation peak at the vicinity of -590 mV corresponding to the oxidation of metallic indium deposited on the surface of n-silicon.

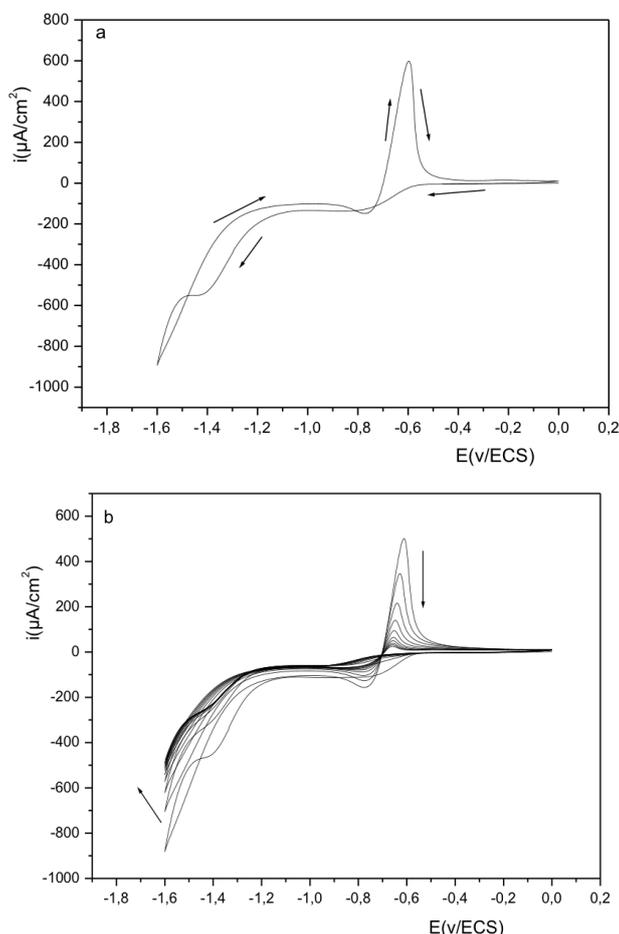


Fig. 1. Electrodeposition of indium on an n-Si (111) electrode ($S = 0.30 \text{ cm}^2$) at $v = 0.1 \text{ V/s}$ and $\text{pH} = 3$, a: one cycle, b: repetitive scanning

The successive scan shows clearly the decrease in the current intensity of anodic and cathodic peaks with a slight displacement of the potential values of the peaks to the most negative. This phenomenon is probably due to the deposition of a passivating layer on the silicon since the first cycle, modifying the electrode surface which becomes less conductive.

Electropolymerization of the monomer (Pyrrole) on the n-silicon

The electrochemical behavior of the monomer has been studied by cyclic voltammetry in acetonitrile organic medium. The electropolymerization of the monomer was performed by anodic oxidation of the monomer.

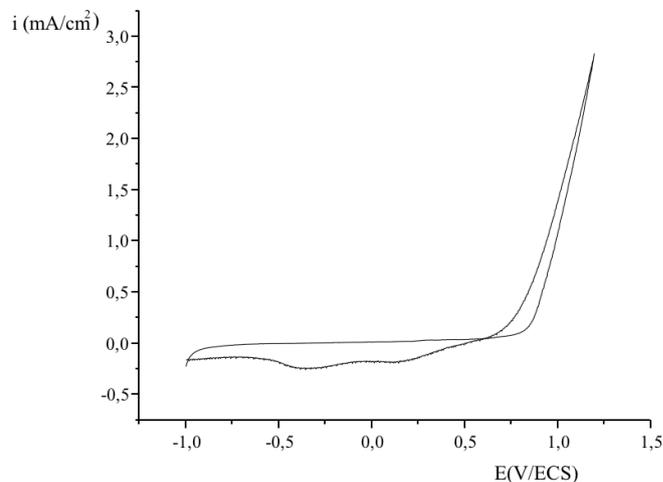


Fig. 2. Cyclic voltammogram of an n-Si (111) electrode in $\text{CH}_3\text{CN } 10^{-1} \text{ M LiClO}_4$ and $4 \times 10^{-3} \text{ M Pyrrole}$, at $v = 0.1 \text{ V/s}$.

An irreversible intense peak observed in the vicinity of 1.2V (fig. 2) corresponds to the oxidation of the monomer into its cation radical which leads to the formation of a polymer film layer. At the feedback scanning, a reduction wave between 0.5 and -0.5 V of the formed polymer has been observed during the polymerization reaction.

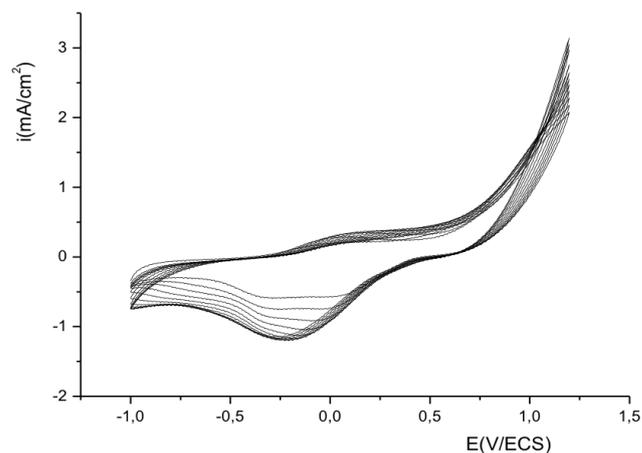


Fig. 3. Repetitive scanning electropolymerization of pyrrole on n-Si (111).

In the successive scanning as shown in Figure 3, we observe an increase of the current intensity in the reduction wave, which confirms the growth of the polymer film deposited on the surface of the n-silicon electrode.

Electrodeposition of indium on polypyrrole by two methods

After deposition of the polymer on the n-type silicon, by electrochemical oxidation of the monomer (pyrrole), we have deposited indium on the polymer (polypyrrole) by a cyclic voltammetry (10 cycles) in a solution of indium chloride

8×10^{-3} M, at pH = 3 (Figure 4).

The obtained curve shows a reduction peak of trivalent indium to metallic indium around -1V, which was deposited on the polymer (polypyrrole) for forming a metallic layer with a shift of the peak towards more positive values and a decrease in current density with the number of cycles.

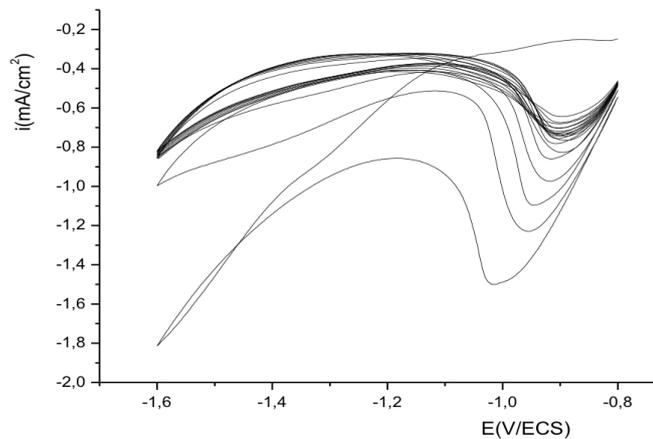


Fig. 4. Direct electrodeposition of indium on polypyrrole/n-Si, with v : 10m V/s and pH =3.

In order to include the indium in the polymeric film, an electrode of n-Si (111) modified by a polypyrrole film was immersed in a solution of indium chloride 8×10^{-3} M for twenty minutes, then electrochemically reduced in an aqueous solution of potassium chloride exempt of In^{3+} ions (figure 5).

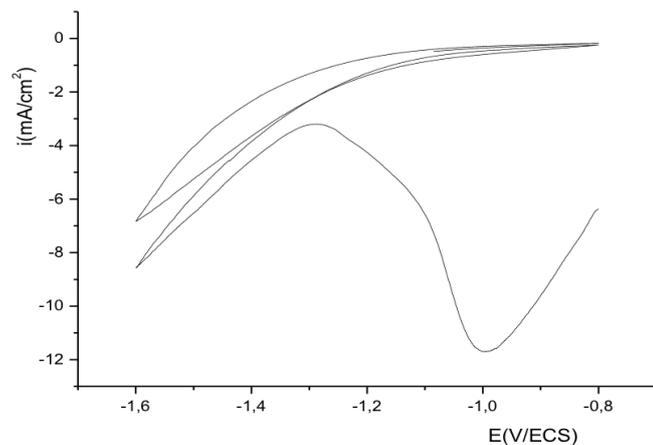


Fig.5. Electrodeposition of indium on n-Si/polypyrrole by scanning at $v = 10$ mV/s after immersion in a solution of indium chloride 8×10^{-3} M, for 20 minutes.

The curve shows the appearance of a reduction peak of trivalent indium to metallic indium in the vicinity of -1 V at the first cycle. All indium cations were reduced since the first cycle, because the second cycle shows no peak. This result confirms the inclusion of indium in the polymer film.

Analysis by atomic force microscopy (AFM)

Figures 6.a and 6.b show the three-dimensional topographical images of electrodeposited indium on silicon electrode modified by polymeric film with both methods.

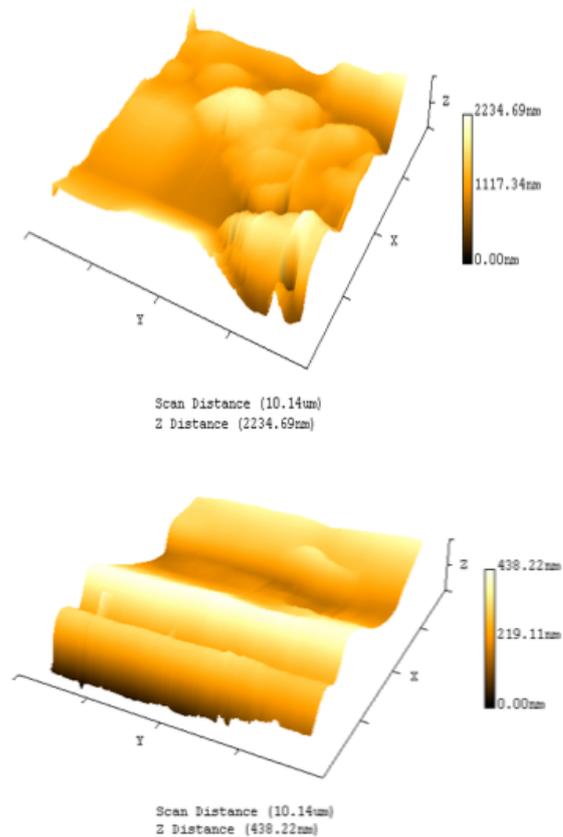


Fig. 6. AFM image of (a) Indium introduced on the modified electrode and (b) indium electrodeposited directly on the modified electrode.

The AFM image in Figure 6.a, corresponding to the deposition method after inclusion of In^{3+} ions within the polymeric film, presents bloatings of height 2234 nm observed on a part of the scanned surface presenting the incorporated indium with a surface roughness of 100 nm.

The AFM image in Figure 6.b, corresponding to the deposition method by direct reduction of In^{3+} ions on the surface of the polymer film, presents waves of height 438 nm observed on the whole scanned surface presenting indium deposited in a thin layer covering the surface of the electrode with a surface roughness of 74 nm.

Conclusion

In this work, the deposition of polypyrrole film on the surface of n-silicon (111) was obtained by electrochemical oxidation of the monomer in an organic medium. The obtained deposit is uniform and covers the entire silicon surface in the monomer solution. The electrodeposition of metal (In) in the polymer film was obtained by two methods: either by direct electroreduction of the metal ions on the material or by inclusion of these ions in the polymer film by simple interaction followed by electroreduction in a solution free of indium ions in order to precipitate metal particles in the polymer film. The electrochemical study showed the inclusion of the metal into the polymer film, due to weak binding between the ions and the polymer. The AFM images obtained by the two methods show the improved state of the electrode surface after inclusion or electrodeposition of the metal.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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