Abstract #123, 224th ECS Meeting, © 2013 The Electrochemical Society

Enhanced photocurrent and crystallinity of modified selenium films with underpotential deposited bismuth or lead

Dyovani Coelho and Sergio A S Machado
Instituto de Química de São Carlos, Universidade de São Paulo
Av. Trabalhador São-carlense, 400, CP 780, São Carlos, São Paulo, Brasil.

The semiconductors play an important role in new technologies such as microchips and photovoltaic cells. One of the key challenges in the manufacturing of the semiconductor materials is its production with a high degree of crystallinity, influencing their conductivity and consequently their applied potential [1]. Usually typical methods require a large energy input in the manufacturing process and expensive equipment, which result in an energy payback time of years. However, we have observed that the production and modification of semiconductor materials, under certain electrochemical conditions, can result materials with high crystallinity and photocurrent response[1].

The proposed electrochemical method involves the underpotential deposition (UPD) as a proper tool to modify, in a totally controlled way, thin semiconductor films aiming to modulate or improve their optical or electrical properties. Thus, a selenium film (f-Se) was obtained by polarization of a gold substrate at -0.40 V (*vs* Ag/AgCl) for 1,800 seconds in a solution containing 0.1 mol L^{-1} HNO_3 + 0.02 mol L^{-1} SeO_2, at 80 °C, under illumination by a halogen lamp (150 W) and magnetic stirring. The temperature has great influence on the structure of the deposit, at temperatures lower than 80 °C is formed a film of amorphous selenium slightly adherent. After, the semiconductor film was modified with ad-atoms of bismuth or lead by application of potential enough for only their underpotential deposition on f-Se for 1,800 seconds, in a 0.1 mol L^{-1} HNO_3 solution containing 1.0 mmol L^{-1} of $Bi(NO_3)_3$ or $Pb(NO_3)_2$, in controlled temperature at 25 ºC.

The produced f-Se at conditions established above presented the characteristics of the trigonal selenium as showed in Figure 1[2]. The X-ray diffraction analysis (XRD) showed characteristic peaks of trigonal selenium and polycrystalline gold substrate phases. However, the modified f-Se with Bi or Pb din't present either metallic phase or alloys such as Bi_2Se_3 or PbSe. This was expected since the amount of deposited metal under conditions of UPD is negligible compared to the amount of selenium.

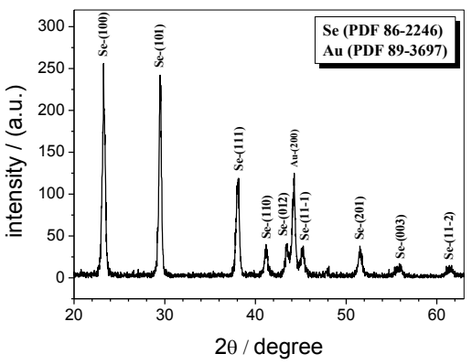
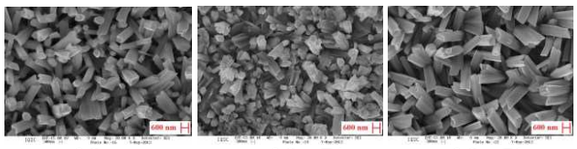


Figure 1: X-ray diffractogram for the electrodeposited selenium on the gold electrode at 80 ºC.

Nevertheless, the voltammetric characterization shows that there is Bi- or Pb-UPD on the f-Se. Moreover, the electrochemical quartz crystal microbalance data provide evidences that there is diffusion of the UPD into the selenium film.

The band gap energies of the semiconductor films calculated from the measurements of diffuse reflectance displayed values near each other. The observed values were 1.93, 1.86 and 1.89 eV for the f-Se, modified f-Se with Bi-UPD (f-Se_Bi) and modified f-Se with Pb-UPD (f-Se_Pb), respectively. Likewise, the images in the Figure 2 show that there are no differences on the morphology between the f-Se and f-Se_Pb, both present microcrystalline structures. Although, the f-Se_Bi presents some deposits in the amorphous form, its cause was not clarified yet.



f-Se f-Se_Bi f-Se_Pb

Figure 2: Images of scanning electron microscopy (SEM).

Furthermore, studies of photocurrent indicated cathodic photocurrent significantly different to all surfaces (Fig. 3). The average responses are -2.03, -16.90 and -4.54 μA cm^{-2} to f-Se, f-Se_Bi and f-Se_Pb, respectively.

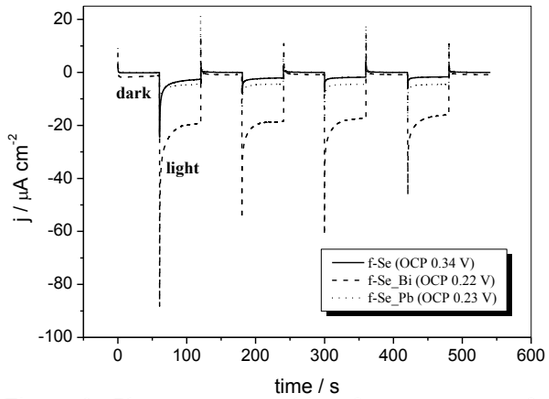


Figure 3: Photocurrent resulting from exposure of the films to 100mW of incident radiation. Measurements performed in OCP for all films in a 0.1 mol L^{-1} HNO_3 solution. Solar Simulator, Newport, lens A.M. 1,5G.

Even though XRD and SEM did not point significant differences between the films, the voltammetric and photocurrent characterizations showed that there are great changes in the behavior between the selenium film and its variation containing ad-atoms of bismuth or lead. Here, we showed a new method for production of selenium films with microcrystalline structures and the possibility of sensitization of its surface with ad-atoms of Bi or Pb increasing its photocurrent response. This new way of semiconductor films production can be used to modulate the optical properties of semiconductor materials, for example.

References

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[3] Steichen, M.; Dale, P. Electrochem. Commun., **13**, 865 (2011).