

## Electrodeposition of Te and Cu Thin Films on Boron Doped Diamond (BDD)

### Electrode.

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In this paper boron-doped diamond (BDD) electrodes were prepared by hot filament chemical vapor deposition (CVD) technique using the standard mixture of H<sub>2</sub>/CH<sub>4</sub>. The boron doping was obtained from H<sub>2</sub> forced to pass through a bubbler containing B<sub>2</sub>O<sub>3</sub> dissolved in CH<sub>3</sub>OH. BDD quality and morphology were characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The electrodeposition of Cu, Te and Cu-Te thin films on BDD electrodes was investigated. Thin films of these metals were deposited potentiostatically from an unstirred, deaerated aqueous solution on BDD and the deposits morphologies were characterized by SEM. Cyclic voltammetry was used to evaluate the electrochemical behavior of BDD electrodes in the deposition and dissolution processes of the Cu, Te and Cu-Te thin films.

### Introduction

Studies on semiconducting copper chalcogenide materials have received much attention because of their potential applications in various devices such as solar cells, superionic conductors, photodetectors, microwave shielding, etc. (1-5). Among these materials the copper telluride compounds exhibit technological interest due to their potential application in thermoelectric devices (6), highly efficient solar cells, photo-diode devices and various hetero-junction electronic components where they are used as p-type semiconductors. Aven and Cusano were the first to make p-Cu<sub>2</sub>Te/n-CdTe hetero-junction solar cells with an efficiency reaching 7.5% (7). Other authors also studied this structure, however, these compounds have rarely been the subject of study, and have been prepared only through dry methods, such as, sputtering and chemical vapor deposition. In this paper the electrodeposition method was used to obtain the Cu, Te and Cu-Te thin films. The ability to grow compact and device quality semiconducting films using electrodeposition presents considerable technological interest. The advantages of method include the fact that most compounds semiconductors are obtained at or near room temperature, which is considered low temperature deposition. Electrodeposition also promotes controlled growth and it is generally a low cost methodology when compared to the dry methods. The cost is the most important factor in making viable photovoltaics for large scale. Besides, BDD electrodes have received great attention due to its unique characteristics such as, inert surface with low adsorption properties, remarkable corrosion stability (even in strong acidic media), and wide working potential window in aqueous

and non-aqueous electrolytes. In this way, this paper is to study the electrodeposition process of Te, Cu, as well as Cu–Te system on BDD electrodes by cyclic voltammetry and its morphological characterization.

## Experimental

The BDD films were grown on Si substrate by chemical vapor deposition (CVD) in a hot filament reactor during 6 hours. It was utilized a gaseous mixture of 99% vol. H<sub>2</sub> and 1% vol. CH<sub>4</sub> with a pressure of 50 Torr. The boron doping was obtained from H<sub>2</sub> forced to pass through a bubbler containing B<sub>2</sub>O<sub>3</sub> dissolved in CH<sub>3</sub>OH. The H<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>/CH<sub>3</sub>OH/H<sub>2</sub> were controlled in order to obtain the desired B/C ratio in CH<sub>3</sub>OH. From the Mott Schottky plot, the doping level was estimated to approximately 10<sup>20</sup> boron atoms.cm<sup>-3</sup> (8). The electrodeposition solutions were prepared by dissolving TeO<sub>2</sub> (Fluka P.A) and CuSO<sub>4</sub> (Dinâmica P.A) in 0.05 mol L<sup>-1</sup> HClO<sub>4</sub> (Merk P.A). All reagents were analytical grade and the water used to prepare the solutions was purified by reverse osmosis system. Prior to the experiments, the solutions were deaerated with N<sub>2</sub> for 10 min. The electrochemical experiments were carried out with a three-electrode system using a microcomputer-controlled Autolab potentiostat/galvanostat model PGSTAT 302. The working electrode was the BDD film with geometric area of 0.2 cm<sup>2</sup>. A platinum wire served as a counter electrode and Ag/AgCl electrode was used as the reference electrode. For the morphologic characterization, Cu, Te and Cu-Te films were deposited onto BDD electrodes at -0.40 V during 30 s. The deposits were characterized by scanning electron microscopy (SEM) images from Jeol equipment JSM-5310.

## Results and discussion

### Electrochemical characterization

Initially, cyclic voltammetry experiments were used to evaluate the deposition and dissolution processes of individual metals. These studies were performed in 1.0 x 10<sup>-2</sup> mol L<sup>-1</sup> CuSO<sub>4</sub> + 0.05 mol L<sup>-1</sup> HClO<sub>4</sub> and 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> TeO<sub>2</sub> + 0.05 mol L<sup>-1</sup> HClO<sub>4</sub> for Cu and Te respectively. Cyclic voltammogram for Cu electrodeposition on BDD electrode is presented in the Figure 1. The electrode potential was swept negatively from 1.0V to -0.65V and then was swept in reverse direction. During the cathodic sweep a defined peak at -0.16V may be observed associated to deposition process of the Cu on BDD electrode. During the sweep in the reverse direction two dissolution peaks (A1 and A2) can be observed. These peaks may be attributed to different Cu interactions with the substrate. The crossover in the cathodic currents that appears on the reverse potential sweep is associated the crossover potential (Figure 1). The presence of this crossover is a diagnostic for the nuclei formation on the electrode. Te deposition on BDD electrode was performed by scanning the potential from 1.0V to -0.65V (Figure 2). Two well-defined peaks were observed at -0.33V (B1) and 0.43V (B2) related to Te deposition and dissolution processes, respectively. For Cu-Te system the electrochemical behavior changed significantly as may be observed in the Figure 3. Analyzing the anodic sweep, it is possible to observe several stripping peaks. Besides the deposition process occurred at different potentials when compared with the electrochemical process of Cu or Te alone. These peaks may be associated to different phases and/or formation of a new compound with contribution of the two metals. Major discussions about anodic peaks need further studies.

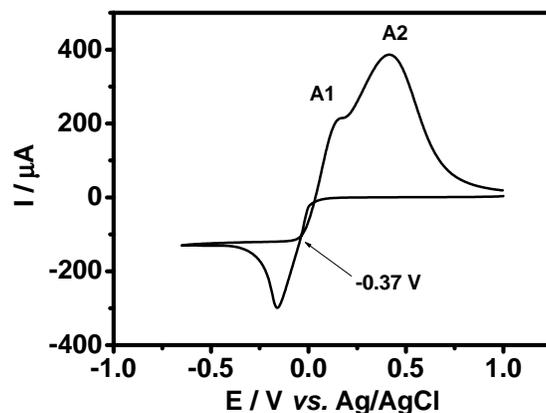


Figure 1. Cyclic voltammogram for Cu electrodeposition on BDD electrode from a solution of  $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ CuSO}_4 + 0.05 \text{ mol L}^{-1} \text{ HClO}_4$ . Scan rate:  $10 \text{ mVs}^{-1}$ .  $A = 0.2 \text{ cm}^2$ .

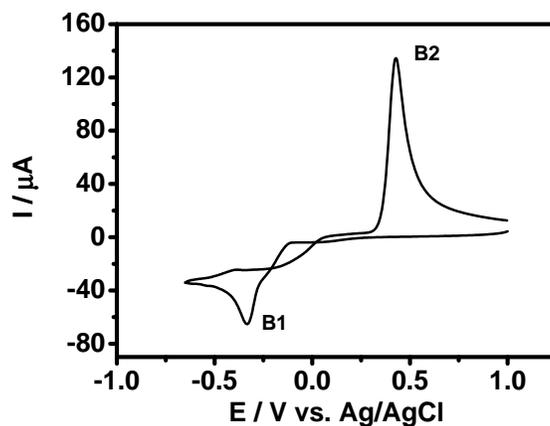


Figure 2. Cyclic voltammogram for Te electrodeposition on BDD electrode from a solution of  $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ TeO}_2$  in  $0.05 \text{ mol L}^{-1} \text{ HClO}_4$ . Scan rate:  $10 \text{ mVs}^{-1}$ .  $A = 0.2 \text{ cm}^2$ .

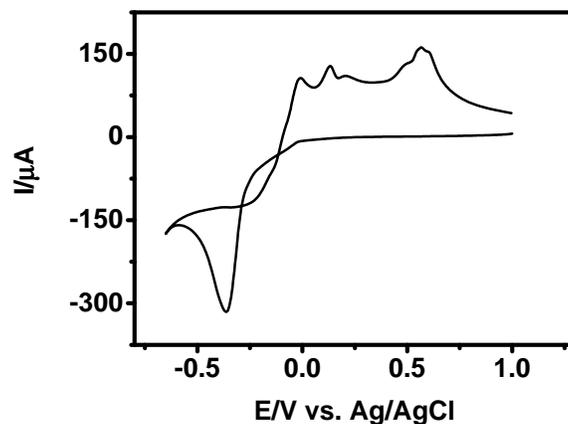


Figure 3. Cyclic voltammogram For Cu-Te electrodeposition on BDD electrode from a solution of  $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ TeO}_2 + 1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ CuSO}_4$  in  $0.05 \text{ mol L}^{-1} \text{ HClO}_4$ . Scan rate:  $10 \text{ mVs}^{-1}$ .  $A = 0.2 \text{ cm}^2$ .

### Surface morphology and Raman spectroscopy

The surface analysis of BDD electrodes made by SEM is shown in the Figure 4. The grains are faceted with symmetrical and smooth faces with uniform texture with predominant (111) orientation. The high population of smaller grain sizes among the bigger ones is an effect concerning to highly doping level of such sample due to the boron incorporation in diamond lattice as an impurity decreasing the film growth rate. Raman spectrum (Fig 4.b) measured at 514.5 nm laser line for the BDD film confirmed the good quality of diamond films because under the present deposition conditions the broad band centered at  $1500\text{ cm}^{-1}$  and attributed to graphite contribution was not identified. The diamond phonon observed at  $1332\text{ cm}^{-1}$  that is a symmetric Lorentzian for undoped film presents a drastic decrease and a downshift to lower energy. Meanwhile, two broad bands appear at  $500$  and  $1230\text{ cm}^{-1}$ . The presence of the  $500\text{ cm}^{-1}$  is attributed to the concentration increase of the boron pairs and the broad band centered at  $1230\text{ cm}^{-1}$  is attributed to the Fano interference between the discrete phonon state and electronic continuum. (9). Following this discussion, the broad peak at  $1230\text{ cm}^{-1}$  should represent the combined peak of single optical phonons caused by the boron incorporation in diamond lattice. Observing the second-order region of the spectrum the highest peak around  $2460\text{ cm}^{-1}$  also appears that correspond well to twice the wave number at  $1230\text{ cm}^{-1}$ . The deposit conditions were chosen from the previous voltammetric experiments. Figure 5 presents the SEM micrographs of Cu (A), Te (B) and Cu-Te system (C) deposited at  $-0.4\text{ V}$  during  $30\text{ s}$ . The morphology of the BDD electrodes change significantly after the film depositions as may be observed. Morphology of the globular type appeared distributed on the sample area when the BDD electrode was modified with Cu electrodeposit (Fig. 5A). For the BDD electrode modified with Te electrodeposit, morphology with dendritic structures was observed (Fig 5B). Otherwise, in the presence of the two metals (Fig. 3C) larger agglomerates are verified and they can be related to copper telluride compound.

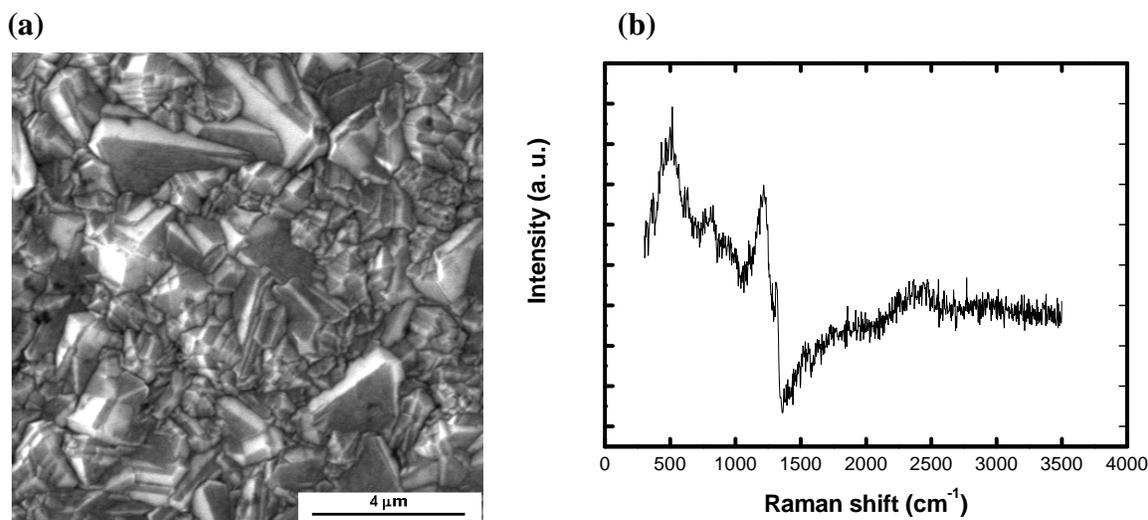


Figure 4. (a) Scanning electron microscopy image and (b) Raman spectrum of the as grown BDD film.

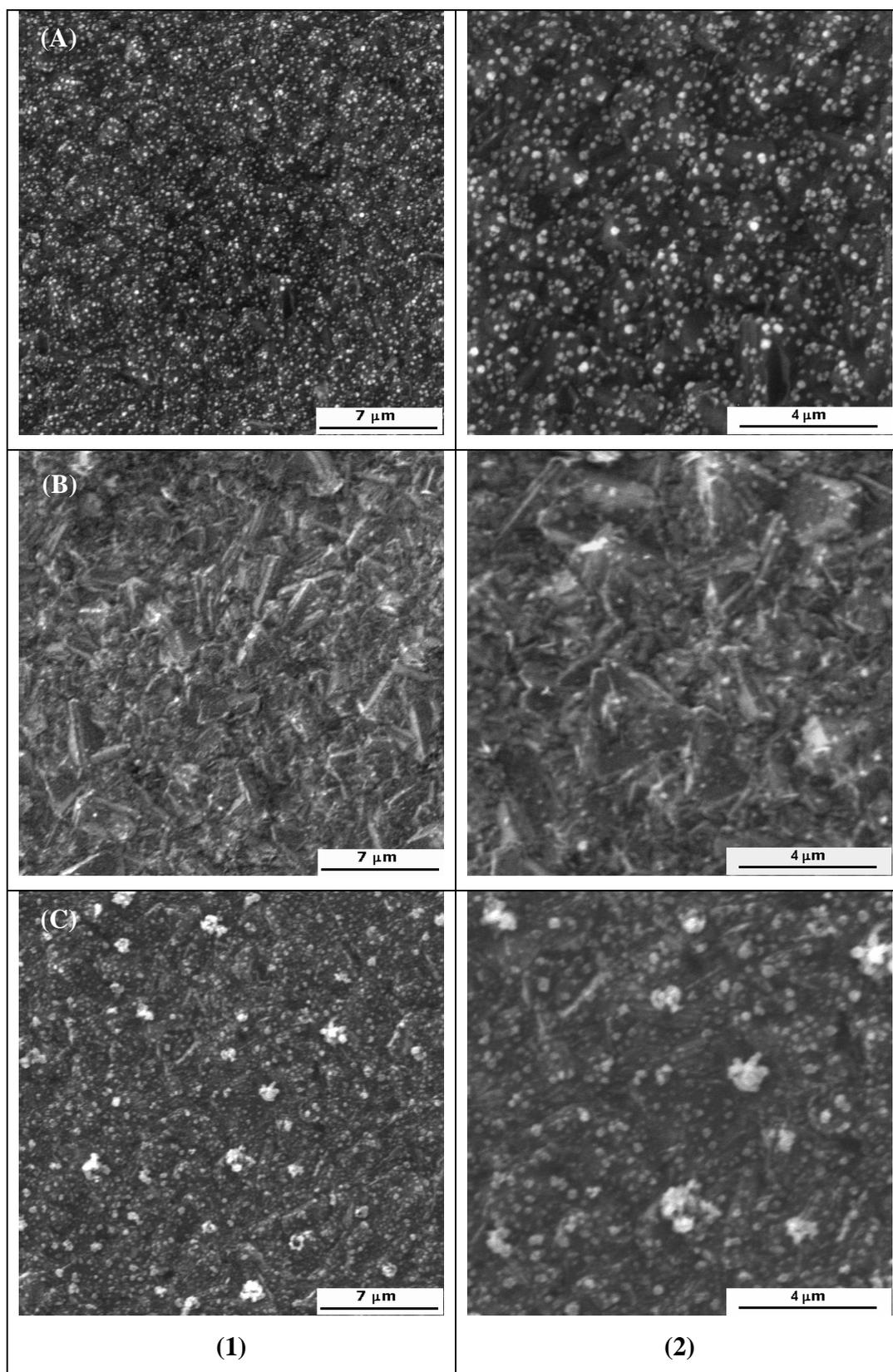


Figure 5. SEM images of Cu (A), Te(B) and (C) Cu-Te system electrodeposits on BDD at -0.4 V for 30 s. (1) 5.000 x and (2) 10.000 x magnifications.  $A = 0.2 \text{ cm}^2$ .

## Conclusions

In this paper the electrodeposition of Cu, Te and Cu-Te thin films on boron-doped diamond electrodes was reported. Raman spectra of the BDD films measured at 514.5 nm laser line for the BDD film confirmed the good quality of diamond films because under the present deposition conditions the broad band centered at 1500  $\text{cm}^{-1}$  and attributed to graphite contribution was not identified. The morphology of the BDD films change significantly after the film depositions. In the presence of the two metals larger agglomerates are verified and they can be related to copper telluride compound. For Cu-Te system the electrochemical behavior changed slightly, the deposition process occurred at different potentials when compared with the electrochemical process of Cu or Te. Through the anodic sweep experiments, it is possible to observe several stripping peaks. These peaks may be associated to different phases and/or formation of a new compound with contribution of the two metals.

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## References

1. W. S. Chen, J. M. Stewart and R. A. Mickelsen, *Appl Phys Lett.*, **46**, 1095 (1985).
2. C. Nascu, I. Pop, V. Ionscu, E. Indra and I. Bratu, *Mater Lett.*, **32**, 73 (1997).
3. H. Okimura, T. Matsumae and R. Makabe, *Thin Solid Films.*, **71**, 53 (1980).
4. H. M. Pathan, C. D. Lokhande, D.P. Amalnerkar and T. Seth, *Appl Surf Sci.*, **218**, 290 (2003).
5. M. A. Korzhuev, *Phys Solid State.*, **40**, 217 (1998).
6. J. W. Gardner, *Engl. Electr. J.*, **18**, 16 (1963).
7. M. Aven and D. A. Cusano, *J. Appl. Phys.*, **35**, 606 (1964).
8. N. G. Ferreira, L. L. G. Silva, E. J. Corat, V. J. Trava Airoldi and K. Iha, *Braz. J. Phys.*, **29**, 760 (1999).
9. R. J. Zhang, S. T. Lee and Y. W. Lam, *Diam. Rel. Mat.*, **5**, 1288 (1996).