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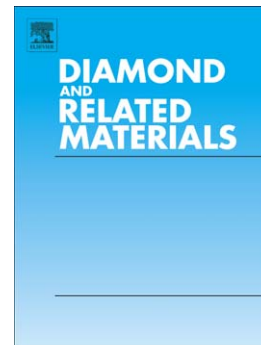
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## A Comparative Study of Copper Electrodeposition and Photoelectrodeposition on Boron Doped Diamond

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### ABSTRACT

Copper (Cu) electrodeposition and photoelectrodeposition on highly boron-doped diamond films (BDD) were investigated, at two different pH solutions. Cu particles were deposited in the potentiostat mode and under UV irradiation. The as-grown as well as the Cu modified BDD films were characterized by Raman Spectroscopy and Scanning Electron Microscopy. The copper photocatalytic deposition on BDD was discussed taking into account the influence of the photogenerated electrons for photoelectrodeposition process at both acid and neutral pH solutions. Under UV irradiation, the copper deposits presented higher density and uniformity all over the crystal faces when compared with those without UV irradiation. This behavior may be attributed to BDD semiconductor character due to its photogenerated electrons which enhanced the copper reduction reaction.

**Keywords:** BDD, copper, electrodeposition, photoelectrodeposition, semiconductor.

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## INTRODUCTION

Boron doped diamond (BDD) has been extensively reported as an excellent material to be applied as an electrode in electrochemical study due to its outstanding features such as: its wide potential window in aqueous solutions as well as its weak adsorption for most types of molecules [1, 2]. However, BDD electrochemical behavior may be improved from the surface modification with deposition of particle metals, which are responsible for increasing its electrocatalytic activity thus increasing its sensitivity and selectivity for electrochemical process.

Due to its extremely wide gap (5.5 eV) and to the fact that the conduction band edge of the semiconductor p-type diamond is located at a very negative potential (-4.27 V versus SHE in 0.1 mol l<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>, pH=4.5), photoelectrochemical behavior has also received much attention [3], partly due to the photogenerated electrons in its conduction band that have a high reducing power [4]. Therefore, it is possible to photoelectrochemically reduce species that are very difficult to reduce under normal conditions. In this sense, BDD photoactivity can be exploited both by photoelectrodeposition of metal ions on its surface and by decomposition of organic and inorganic substances from contaminated water [5, 6].

Pleskov et al. were the first researchers to examine diamond photoelectrochemical response and they keep one working in this area [7-9]. The first demonstration of the electron excitation from the valence band to the conduction band was published in 1997 by Boonma et al. [10]. They reported that it was possible to photoelectrochemically generate hydrogen gas on diamond at overpotential of -1.8 V. Rao et al. [11] showed surface treatment influence on the diamond photoelectrochemical properties, which improves when its surface is oxidized. Zhong et al [12] studied the photoelectrochemical diamond efficiency and discussed its superior performance compared to other semiconductors in the process of functionalization with bithiophenedicyano molecules.

Several studies concerning copper deposition processes have been reported, such as, photoelectrodeposition [13], sputtering [14], electrodeposition [15], PVD-processes [16] wetness technique [17] and electroless deposition [18]. Among these methods, electrochemical deposition offers good filling capability, low-cost, and it is a fast alternative process to produce copper particle modified electrode. Moreover, several studies have confirmed that the photo-assisted metal deposition method is very useful for the preparation of efficient electrode material [19]. The last two techniques together provide an interesting research line in the metal deposition process. Thus, this work aims at doing a comparative

study between copper electrodeposition and photoelectrodeposition onto BDD films in two different pH solutions, acid and neutral. In this study, basic pH is not used because the solubility of Cu (II) salts is limited in basic solutions due to the formation of hydroxide, which is insoluble in water.

Here we discuss the influence of the photogenerated electrons to understand the copper photocatalytic deposition in diamond films. To the best of our knowledge there is no work in the literature that discusses the influence of pH in Cu photoelectrodeposition process.

## EXPERIMENTAL

The films were grown by hot filament-assisted chemical vapor deposition (HFCVD) technique with the following growth parameters: 780 °C, 50 Torr, 14 h and gas mixture 1/99 % of CH<sub>4</sub>/H<sub>2</sub>. The films were deposited on silicon substrate after a seeding pre-treatment [20]. Boron source was obtained by an additional hydrogen line passing through a bubbler containing B<sub>2</sub>O<sub>3</sub> dissolved in methanol. The doping level corresponds to the acceptor densities of around 10<sup>21</sup> atoms cm<sup>-3</sup> estimated from Raman's measurements. Electrochemical measurements were carried out using the Autolab PGSTAT 302 equipment with a standard three-electrode, in a single-compartment glass cell with a quartz window. The geometric area of the diamond films in contact with the electrolyte was 0.13 cm<sup>2</sup>. A platinum wire served as a counter electrode and Ag/AgCl/KCl<sub>(sat)</sub> was used as the reference electrode. Prior to the electrodeposition and to the photoelectrodeposition, the films were exposed under UV irradiation during 2h to promote the oxygen functional groups that serve as anchor points for Cu deposited thus improving the interfacial adhesion between BDD films and the metal coating [21]. Firstly, the electrochemical and the photoelectrochemical study of the copper process was performed by cyclic voltammetry at a scan rate of 100 mV s<sup>-1</sup> in an electrolyte 50 mmol l<sup>-1</sup> HClO<sub>4</sub> and 50 mmol l<sup>-1</sup> NaClO<sub>4</sub> containing Cu<sup>+2</sup> at a constant concentration of 1 mmol l<sup>-1</sup> CuSO<sub>4</sub>. All the solutions were prepared with deionized water and then deoxygenated by bubbling N<sub>2</sub> during 30 min before the beginning of each series of measurements. The electrodeposition and the photoelectrodeposition of Cu particles on diamond films were performed under potentiostatic mode, at a fixed potential of -0.6 V for a time of 10 min in the solution described above, under and without ultra-violet (UV) irradiation. During the deposition process, no pH change was observed.

The light source was a home-made system, composed of a set of five commercial lamps (Philips TUV 30 W/G30T8) placed in a closed box. The UV irradiance at the electrode

position was  $12 \text{ W/m}^2$  measured by a radiometer. For both electrodeposition and photoelectrodeposition procedures, the solution was purged with  $\text{N}_2$  30 min before starting and kept during the experiments. The Cu modified diamond films morphology was verified from the scanning electron microscopy (SEM) images using a Jeol JSM-5310 microscope.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Morphological and Structural Characterization of the BDD electrode

Figure 1 shows the Raman's scattering spectrum of the BDD film. The characteristic Raman peak at  $1332 \text{ cm}^{-1}$  corresponds to the vibration of a diamond first-order phonon, and confirms the quality of this BDD film. The effect of boron doping is reflected in the spectral features. The peak of the diamond ( $1332 \text{ cm}^{-1}$ ) shifted to lower energies due to tensions caused by boron incorporation in diamond lattice, and this peak decreased in intensity due to the high B content in it. In addition, two bands located at  $500 \text{ cm}^{-1}$  and  $1220 \text{ cm}^{-1}$  appeared [22]. More recently, Niu et al. [23] have discussed the electronic and vibrational properties of heavily BDD. They concluded that the  $500$  and  $\sim 1220 \text{ cm}^{-1}$  bands are both superposed bands, including not only C vibrations but also B-B vibrations and B-C vibrations, respectively. The boron concentration in diamond film was estimated from the fitting of  $500 \text{ cm}^{-1}$  peak using a combination of Gaussian and Lorentzian lines [24]. The acceptor concentrations were evaluated at around  $10^{21}$  boron atoms  $\text{cm}^{-3}$  for this electrode. The high doping level of this film is clearly observed in Figure 1 where the band at  $1220 \text{ cm}^{-1}$  is higher than that of the diamond peak not to mention its evident second order feature at around  $2500 \text{ cm}^{-1}$ .

The top view SEM image (not shown) of the diamond film deposited on the Si substrates shows that the BDD film grew with a continuous and uniform surface morphology covering the whole substrate without delamination or cracks, characterized by well-shaped microcrystalline grains. It presents sharp facets and crystallographic orientation varying between  $\langle 111 \rangle$  and  $\langle 100 \rangle$ .

It is important to notice that after UV pretreatment and at different pH solutions, changes in the BDD film quality and morphology were not observed. These results are in agreement with SEM images and Raman spectra (not shown).

### 3.2. Electrochemical responses of diamond films in the copper electrodeposition

An important experimental parameter to be considered in the electrodeposition and photoelectrodeposition processes is the influence of the electrolyte composition in the BDD/electrolyte interface. In this work, the electrochemical behavior of Cu was investigated in two different electrolytes ( $\text{HClO}_4$  and  $\text{NaClO}_4$ ) in order to evaluate the influence of the pH in both Cu deposition processes on the BDD electrode. A cyclic voltammetry at  $100 \text{ mV s}^{-1}$  was performed in the absence and under UV irradiation to characterize the Cu reduction and oxidation processes on the BDD surface in the two media above cited. This procedure is important to choose the potential to be applied during the deposition study. Cyclic voltammograms of Cu on BDD films in  $1 \text{ mmol L}^{-1} \text{ CuSO}_4 + 50 \text{ mmol L}^{-1} \text{ HClO}_4$  and  $1 \text{ mmol L}^{-1} \text{ CuSO}_4 + 50 \text{ mmol L}^{-1} \text{ NaClO}_4$  aqueous solutions, in the absence and under UV irradiation are presented in the Figure 2.

The processes of deposition and of dissolution are evident. However, it is noted that these results were influenced by the pH of the medium and by the presence of UV irradiation. The Cu cyclic voltammogram obtained using acid solution, and in the absence of UV light (Figure 2a) showed that during the scan toward negative potentials, the cathodic current starts to increase around  $-0.34 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$ . This is associated with the onset of the Cu deposition and the decrease of current at  $-0.5 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  is due to the diffusion process. In the reverse potential scan, two crosses were observed. According to the theory developed by Fletcher *et al.* [25], the more cathodic crossing at  $-0.38 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  is characterized as the nucleation potential ( $E_n$ ), whereas the second crossing, at  $0.04 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  indicates the reversible potential ( $E_{\text{rev}}$ ) of the  $\text{Cu}^{2+}/\text{Cu}$  system. In more positive potentials, the appearance of two peaks current at  $0.1$  and at  $0.3 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  indicates the Cu dissolution corresponding to the various phases of Cu deposited during the negative potential sweep. By using neutral solution, the Cu deposition occurred at  $0.01 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  which corresponds to a more positive region compared to that made in acid medium indicating a more favorable energy condition for this process. In the reverse potential scan a cathodic current is still observed, but the nucleation loop is not noticed. For the potential at  $0.04 \text{ V}$  and at  $0.3 \text{ V x Ag/AgCl/KCl}_{(\text{sat.})}$  the Cu dissolution was verified.

It is interesting to point out that under UV irradiation, there was a shift to a more positive potential with respect to the Cu reduction for both pH values. This behavior may be

associated with favoring the Cu deposition on the BDD by photogenerated electrons at the electrode surface.

As it can be seen in Figure 2 A, in acid medium, during the scan toward negative potentials, it is observed an abrupt increase in the cathodic current at around  $-0.7 \text{ V} \times \text{Ag/AgCl/KCl}_{(\text{sat.})}$  which is associated to hydrogen evolution. Conversely, in neutral medium, Figure 2 B, such evolution is not observed. The hydrogen evolution probably causes a slight change on diamond surface termination from oxygen to hydrogen termination. We observed in previous work [21] that the deposition and the consolidation of Cu particles on BDD electrode are strongly affected by hydrogen or by oxygen. It is observed that the BDD film treated with hydrogen plasma presented a lower copper adherence while for the BDD film treated with oxygen plasma an increase in the Cu adherence was noticed. This behavior was associated to the formation of hydroxyl, carboxyl and carbonyl groups that serve as an anchor point for Cu particle. Taking this into account, the observed shift difference between the oxidation peak in acid and in neutral solution is associated with these terminations. Due to the weak adherence of Cu on the surface with hydrogen termination, the energy necessary to Cu dissolution is lower when compared to that required on the surface functionalized with oxygen termination.

Considering the Cu electrochemical process presented above, the potential chosen for the deposition was  $-0.6 \text{ V}$ , which certainly guarantees the deposits for both deposition processes.

### ***3.3. Copper particles electrodeposition and photoelectrodeposition***

The surface modification with Cu particles resulted in a morphology composed of rounded grains distributed throughout the surface for all the BDD films as it can be seen in Figure 3.

SEM analysis of the images (B) and (D) under UV irradiation showed that the copper deposited was more uniform and with higher particle densities than those for images (A) and (C) (without UV irradiation). On the other hand, for images (A) and (C) the electrodeposits seem larger and randomly located on the BDD surface with lower particle density. This morphological difference between electrodeposition and photoelectrodeposition may be explained by the semiconductor character of the BDD films. The BDD surface presents high diamond purity where the conductivity is due to the boron excess at the top of its valence band. Therefore, the photoassisted process by UV irradiation generated additional electrons at the conduction band that could participate in the Cu electroreduction. In addition, the positive holes in the valence band may oxidize the water to molecular oxygen or to hydroxyl radicals. Particularly, the BDD represents a class of semiconductor with a wide band gap, where the

recombination of the electrons is lower compared to that of conventional semiconductors [12]. Thus, this excess of electrons in the conduction band enhances the Cu deposition. Considering the different electrolytes used in this work, the possible reactions that may occur in the photoassisted process are summarized in Table 1.

It is interesting to highlight that a better Cu photoelectrodeposition process was obtained by using neutral solution. These results were confirmed in the EDS measurements. The EDS spectra, indicate that in the neutral solution the Cu content was of 4.54 wt.% whereas in the acid solution the Cu content was of 2.76 wt.%.

These results may be attributed to the more favorable energetic condition of the Cu reduction on neutral medium as it can be seen in the cyclic voltammograms (Figure 2b). Moreover, a competition may occur between the  $H^+$  and the  $Cu^{2+}$  by the electron photogenerated, since the  $H^+$  can also be photoelectroreduced on the semiconductor diamond surface [10, 11]. As it can be seen in Table 1, in neutral medium there is a smaller amount of  $H^+$  available so that its reduction occurs forming hydrogen gas. So, the photogenerated electrons are captured by  $Cu^{2+}$ , increasing the copper deposit on the BDD surface.

## CONCLUSIONS

This study showed that the copper electrodeposition process on semiconductor diamond surface is strongly affected by the UV irradiation and by the solution pH values. Cyclic voltammetry results for copper deposition on BDD made in neutral medium showed that the initial potential for cathodic current happened earlier than that in acid medium, evidencing a more favorable energetic condition for this process. Furthermore, under UV irradiation, the Cu reduction process occurs at a more positive potential for both pH values. By applying UV irradiation, the copper photoelectrodeposited presented high density and was uniformly distributed all over the crystal faces. This behavior was attributed to the additional generated electrons at the conduction band, where the recombination process on BDD was low and, consequently, ensured an increase in the density of copper deposits. Concerning the different pH solutions, the neutral medium was more efficient in relation to the copper photoelectrodeposition process. This result was associated with the lower competition between the  $H^+$  and the  $Cu^{2+}$  by the photogenerated electron.

## ACKNOWLEDGMENTS



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**Figure Captions**

**Figure 1-** Raman spectrum of the BDD electrode.

**Figure 2-** Cyclic voltammograms of Cu on BDD electrode obtained in two different supporting electrolyte: (a)  $1 \text{ mmol l}^{-1} \text{ CuSO}_4 + 50 \text{ mmol L}^{-1} \text{ HClO}_4$ ; (b)  $1 \text{ mmol l}^{-1} \text{ CuSO}_4 + 50 \text{ mmol L}^{-1} \text{ NaClO}_4$ .

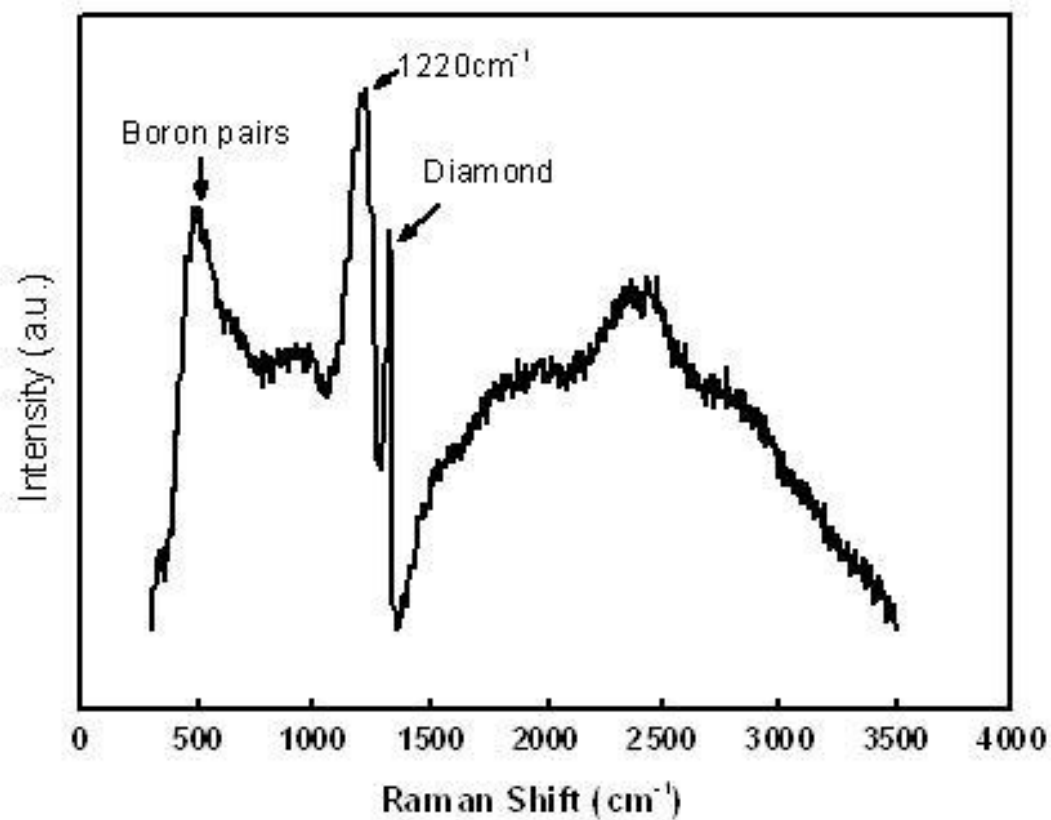
**Figure 3-** SEM images of BDD after Cu particle deposition. (A)  $\text{HClO}_4$ , (B)  $\text{HClO}_4$  under irradiation, (C)  $\text{NaClO}_4$ , (D)  $\text{NaClO}_4$  under irradiation.

**Table 1-** Possible reactions in the photocatalytic process of the diamond: (a)  $\text{HClO}_4$ , (b)  $\text{NaClO}_4$ .

Table 1

(a) In acid solution (1 mmol L <sup>-1</sup> CuSO <sub>4</sub> + 50 mmol L <sup>-1</sup> HClO <sub>4</sub> )	
$\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$	(1)
$\text{HClO}_4 \rightarrow \text{H}^+ + \text{ClO}_4^-$	(2)
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	(3)
$h\nu \rightarrow h^+ + e^-$	(4)
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	(5)
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	(6)
$\text{OH}^- + h^+ \rightarrow \cdot\text{OH}$	(7)
(b) In neutral solution (1 mmol L <sup>-1</sup> CuSO <sub>4</sub> + 50 mmol L <sup>-1</sup> NaClO <sub>4</sub> )	
$\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$	(8)
$\text{NaClO}_4 \rightarrow \text{Na}^+ + \text{ClO}_4^-$	(9)
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	(10)
$h\nu \rightarrow h^+ + e^-$	(11)
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	(12)
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	(13)
$\text{OH}^- + h^+ \rightarrow \cdot\text{OH}$	(14)

Figure 1



AC

Figure 2

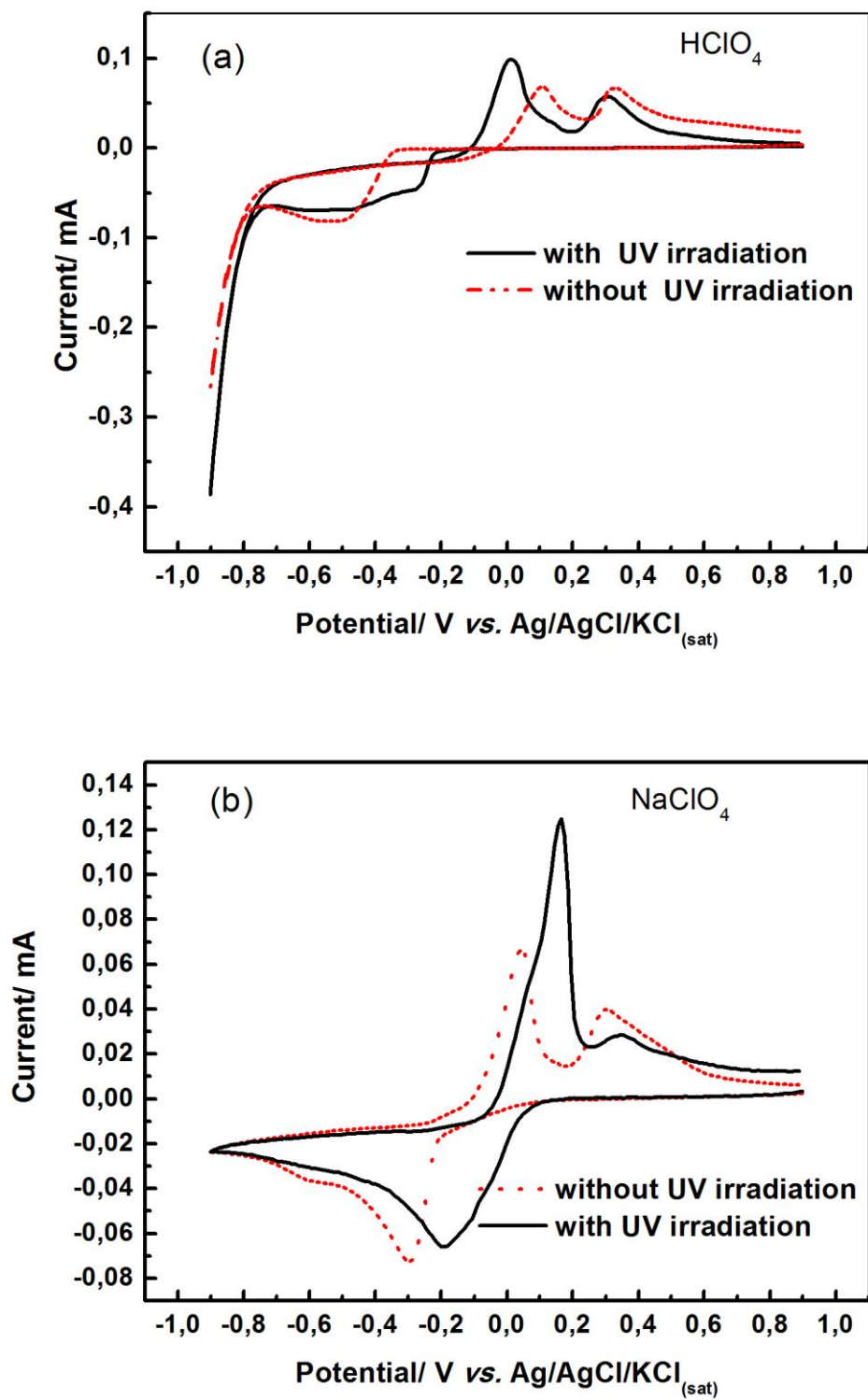
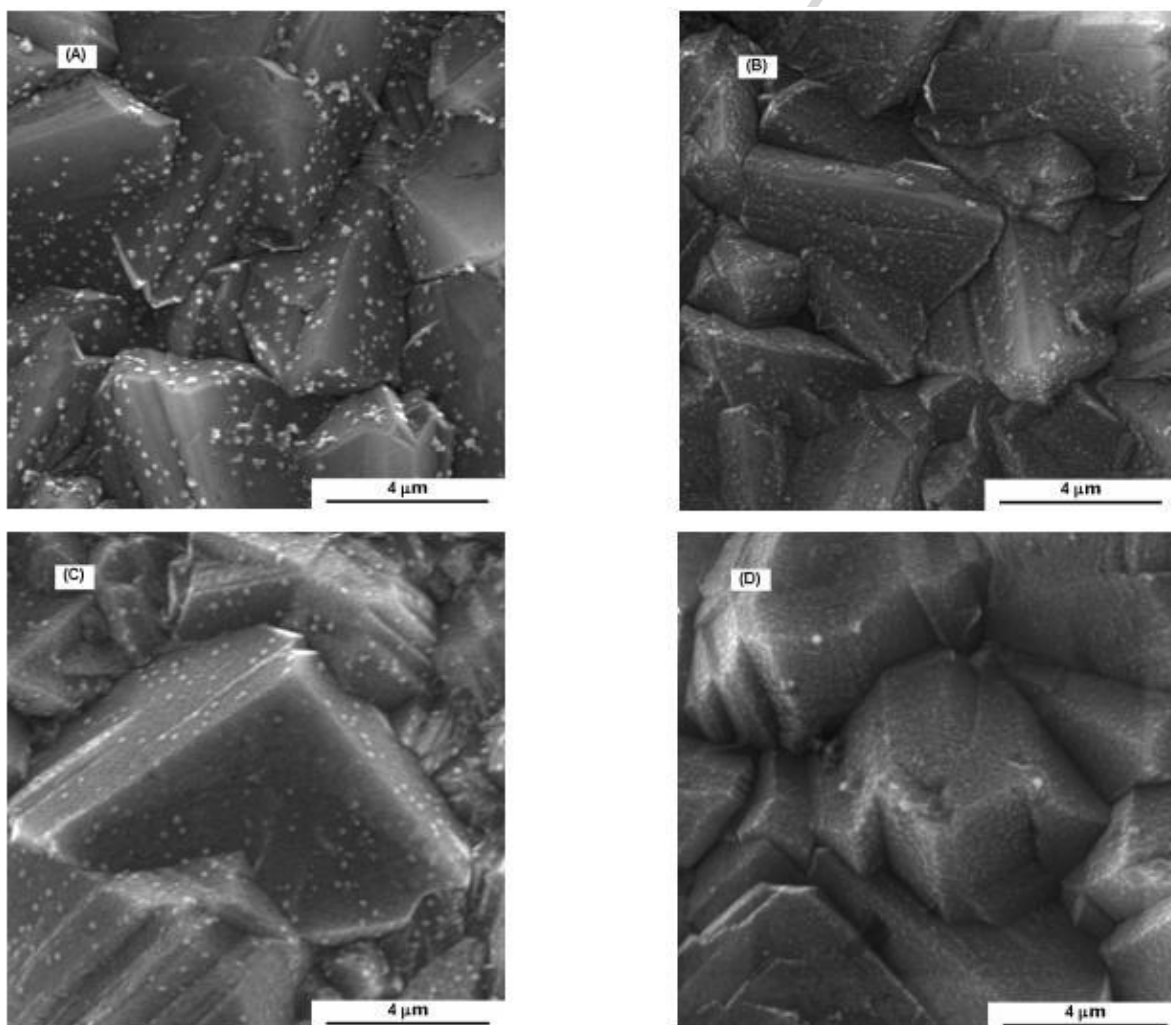


Figure 3





**Prime Novelty**

Copper particles were deposited by using electrodeposition and photoelectrondeposition on boron doped diamond films. The influence of the photogenerated electrons shows a strong influence on the copper photocatalytic deposition on diamond films. The copper deposits presented high density and uniformity all over the crystal faces.

**Highlights**

- Electrodeposition and photoelectrodeposition of copper on boron-doped diamond were obtained.
- The influence of the photogenerated electrons to understand the copper on the diamond film was discussed.
- The copper deposited presented high density and uniformity all over the crystal.