The structure and electrochemical properties of BDD deposited on the Ti-substrate with Ta buffer layer

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Abstract. In this paper, boron doped diamond (BDD) thin flms have been deposited on Ti-based substrates with or without a Ta intermediate layer by microwave plasma chemical vapour deposition (MWCVD). Raman spectroscopy and scanning electron microscopy (SEM) examinations demonstrate that the electrode has well-defined diamond features. XRD spectroscopy shows no TiC in the BDD film on the Ti substrate with Ta buffer layer. It is observed that both the BDD electrodes have similar overpotential 2.5V for water electrolysis prohibiting the evolution of oxygen in the cyclic voltammetry test. Further more，the removal efficiency of chemical oxygen demand (COD) approaches to 100% in the electrochemical oxidation of wastewater containing phenol.

1. Introduction

Industrial effluents contain a wide variety of pollutants, including biorefractory organic compounds which resist conventional treatment techniques and are harmful to the environment and human beings [1, 2]. Recent research has shown that boron-doped diamond anode (BDD) electrochemical technique can offer a good opportunity to prevent and remedy pollution problems [3, 4].The electrochemical properties of BDD deposited on Si, Ti, Ta substrate have been reported[5,6,7]. However, friable Si and expensive Ta are not suitable to commercial manufacture. Ti is an attractive substrate material for the BDD film electrodes due to the compromise between material cost, corrosion and mechanical stability [6]. On the other hand, the porous and loose TiC between the interface of Ti substrate and BDD leads to the adhesion decreasing.

This work aims to solve the problems above, in which a nanometers Ta film was deposited on the Ti substrate as buffer before the BDD film deposition to prevent the formation of TiC. The electrochemical oxidation of 2, 4-dichlorophenol at BDD electrode is to evaluate the potential application of this electrode material for the electrochemical treatment of wastewater containing phenol.

2. Experimental detail

The BDD thin films were deposited on Ti and Ti/Ta wafers by means of microwave plasma-assisted chemical vapour deposition at 1.7KW, 4.7KPa, the Ti/Ta wafer was that a nanometers Ta film was deposited on the Ti substrate by magnetron sputtering at 100W, 0.3Pa. The phase and crystal structure of the as-deposited BDD films were identified by using X-ray diffractometry (XRD)、scanning electronic microscope(SEM) and Raman. Electrochemical measurements were performed in a conventional three-electrode cell at room temperature. BDD electrodes of 1 cm2 area were used as working electrodes in the cyclic voltammetric measurements,

saturated calomel electrode (SCE) as a reference electrode and Pt electrode as counter electrode. Voltammetry experiments were performed in unstirred solutions (200mL). The anode was anodically polarized for 5min with a 1M H2SO4 solution at 0.1A prior to each experiment. The cyclic voltammograms were recorded with a 2273 poterntiostat, a potentiostat/galvanostat was used for the potentiostat electrolysis. Chemical oxygen demand (COD) was determined by the GDYS-101SQ CODCr analyzer (Jilin University Little Swan Instruments Co. Ltd).

3. Results and Discussion

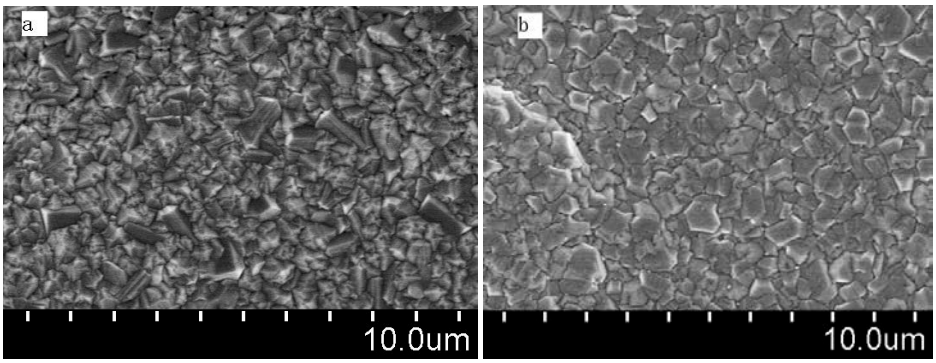

Fig.1 SEM images of BDD film electrode deposited on different substrates
(a) Ti; (b) Ti/Ta

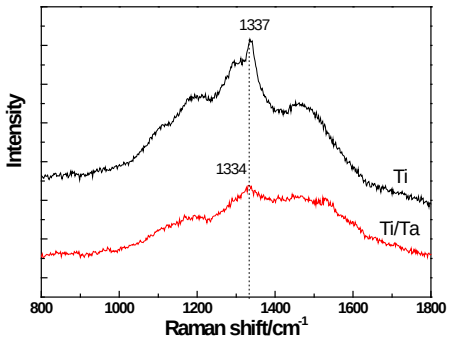

Fig. 2 Visible Raman spectrum of BDD film electrode deposited on Ti and Ti/Ta

Fig.1 shows the SEM images of BDD film electrode deposited on different substrates. The deposited BDD films exhibit well faceted crystallites with typical size in the range of 0.5–1.5μm. The BDD film on the Ti/Ta has a smoother surface than that on Ti substrate. The structure of the different layers was determined by Raman and XRD measurements. The phase purity of BDD films grown on the Ti and Ti/Ta substrates was revealed by Raman spectroscopy (shown in Fig. 2). The Raman peak positions of BDD on Ti and Ti/Ta are 1337 and 1334cm-1 respectively, which are systematically shifted toward higher values relative to that of 1332cm−1 known for unstressed single crystal diamond. The Raman peak shift also reflected the stress in the film. Thermal compressive stress could be generated in diamond film due to the mismatch between the thermal expansion coefficient of diamond and Ti substrate. This stress results in the peak shift to higher frequencies. The correlation between the biaxial stress σ and the Raman peak position shift Δν, in a polycrystalline diamond film, is given as [8]

$$\sigma = -0.345\text{GPa/cm}^{-1}\,\Delta\,\nu$$

The calculated stress of BDD on Ti and Ti/Ta are1.553GPa and 0.518GPa, which means that the Ta buffer is benefit to decrease the residual stress between the BDD film and Ti substrate.

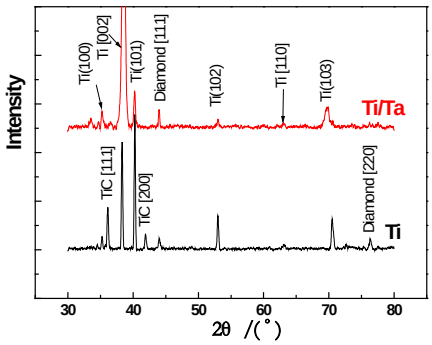

Fig.3 XRD spectrum of BDD film electrode deposited on Ti and Ti/Ta

Fig.3 shows the XRD spectrum of BDD films on Ti and Ti/Ta substrate. The XRD spectra of the respective samples reveal the presence of diamond with major diffraction peaks corresponding to that of the (111) and (220) planes of the diamond JCPDS 89-3441 standard. Presence of titanium carbide TiC (111) and (200) planes is also observed in BDD film on the Ti substrate. It is noted that the BDD film grown on the Ti/Ta substrate, the TiC planes eliminate due to the Ta buffer which prevents the formation of TiC, and the diamond lines relative intensity (111) is stronger comparing with that of the films grown on the Ti substrates, while, the relative intensity of diamond (220) formed hardly on Ta [7] is much weaker. Peak of Ta(β -002) is found at 33.54° in Fig.3 due to the deposition condition of magnetron sputtering[9]. Peaks of α -Ta(101) and Ti(002) are not able to distinguished due to their superposition[10].

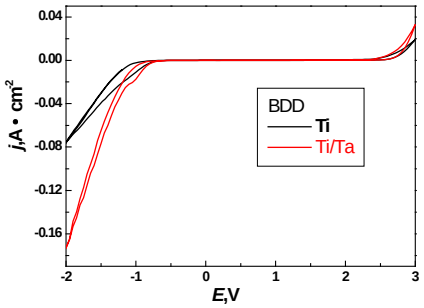

Fig.4 Cyclic voltammorgrams of BDD electrodes in 1molL-1 H_2SO_4 solution

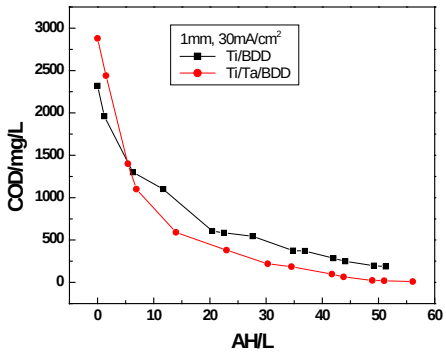

Fig. 5 Variation of COD removal efficiencies as a function of total charge density during dichlorophenol potentiostatic oxidation. current density 30mA/cm2;Na2SO4 addition 20.0 g/L; 40 ℃; pH 8.0;.

Fig.4 shows the cyclic voltammorgrams of BDD electrodes in 1molL-1 H2SO4 solution. The cyclic voltammetric experiments are performed at a sweep rate of 50mVs-1 within -2V~3V. Both the

BDD electrodes possess a wide potential window of ~ 3.2 V, which is typical of polycrystalline BDD films deposited on Ti [6].The background current is estimated in the mid-window of the voltammogram of the respective BDD electrode. The results reveal an excellent integrity of the high quality film that virtually expose to electrochemical reactions. The low background current of <10μA cm−2 for the both BDD electrodes on Ti and Ti/Ta evidences the practical absence of the surface side-reactions. This also implies a high corrosion stability of the electrodes. It must be noted that water decomposition cannot be avoided for BDD on Ti or Ti/Ta, when the electrode potentials are higher than O2 evolution potentials. With the increase of electrode potential, the water decomposition takes place more severe on BDD with Ta buffer film, this indicates that the potential applied on the electrodes ranged from -0.7V to 2.5V, which is sufficient for the potential to discompose the most organic compound by electrochemical oxidation is less than 2.0V [2]. Fig. 5 shows the decay of COD value for wastewaters containing 2, 4-Dichlorophenol. It is seen that high concentration COD value of ~2400mgL−1 is easily decomposed on BDD surface, so that the organic compound in wastewater is oxidized completely. The COD removal efficiency is almost 100%. It is observed that the COD removal velocity of the BDD electrode on Ti/Ta substrate is higher than that on Ti, which also implies that a faster degradation could be obtained on BDD electrode with a Ta buffer film.

4. Summary

The BDD electrodes have been synthesized on Ti or Ti/Ta substrates, the intermediate Ta layer is benefit to prevent the formation of TiC between the Ti and BDD film. The removal efficiency of COD for wastewaters containing 2, 4-Dichlorophenol by BDD is almost 100%. The BDD on Ti/Ta substrate shows higher degradation velocity and is a promising electrode for the treatment of industrial wastewater.

References

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