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Characterization of Oxygen-terminated Diamond Electrodes for Electrochemical Applications

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Contents

List of Figures

List of symbols

C	capacitance
C_{DL}	double-layer capacitance
C_{SC}	depletion-layer (space charge) capacitance
$\underline{C}$	complex capacitance
c_0	reference concentration
c_b	bulk concentration in electrolyte
$c_{H_3O^+}$	H_3O^+ concentration
D	diffusion constant
d_A	thickness of layer A
d_{CO}	thickness of C-O-layer
$d_{\alpha C}$, $d_{\alpha C1}$, $d_{\alpha C2}$	thicknesses of α-C layers
E	energy
E_a	activation energy of dopants
E_b	binding energy
E_g	bandgap
E_{kin}	kinetic energy
F	Faraday constant
f	measurement frequency
h	Planck constant
I_A, I_B	intensities
I_{A0}, I_{B0}	maximum intensities
J	current density
J_0	exchange current density
k_B	Boltzmann constant
m^*	effective mass
N_A	acceptor concentration
n	n-factor of constant phase element

$n(x)$	charge carrier profile
Q	charge
Q_0	nominal capacitance of constant phase element
q	elementary charge
R_1	resistance
R_{CT}	charge-transfer resistance
R_{DL}	double-layer resistance
R_g	gas constant
R_{GB}	resistance across grain boundaries
R_{SC}	depletion layer resistance
r_0	radius of microelectrode
s	scan rate
T	absolute temperature
t	time
V, V_s	electrode potential
V_0	equilibrium potential of redox reaction
V_{FB}	flatband potential
V_{OCP}	open-circuit potential
Z	impedance
$\underline{Z}$	complex impedance
z	number of exchanged electrons
α	transfer coefficient
β_A	surface coverage with layer A
ϵ_0	dielectric constant
ϵ_r	relative permittivity
λ	escape length of photoelectrons
ν	frequency (X-rays)
θ	detection angle
Φ_{det}	work function of photoelectron detector
Φ_{SC}	potential drop across depletion layer
ϕ_B	electronic surface barrier
ω	circular frequency

Abstract

The topic of this thesis is the electrochemical characterization of oxygen-terminated single-crystal- and nanocrystalline diamond electrodes. Diamond is a very attractive material for bio- and electrochemical applications due to its exceptional stability, its biocompatibility, and its electrochemical properties like wide potential window of water dissociation and low background current. The oxygen-termination improves the stability of the electrode characteristics, which is the main advantage compared to the hydrogen termination, which is apparent directly after growth.
However, the characterisitcs of oxygen-terminated diamond electrodes are very dependent on the oxidation treatment, as it is shown in this work. Four different oxidation treatments are investigated by electrochemical measurements: Wet-chemical oxidation in a H_2SO_4/H_2O_2 mixture, anodic oxidation in KOH, RF oxygen plasma without DC bias and an etching process in argon/oxygen plasma including a DC bias. The electrode characterisitcs are correlated with the results from X-ray photoemission spectroscopy (XPS) measurements. It is shown that these oxidation treatments induce different carbon-oxygen functional groups on the diamond surface. In addition, plasma treatments can lead to sp^2-like defects, especially in the case of the argon/oxygen etching process. In the latter case, the plasma process results in a thin layer of non-diamond phases, which is expected to degrade the performance of the diamond electrodes exposed to this treatment. The different carbon-oxygen surface groups and the different amounts of sp^2-like defects have a significant influence on the electrochemical characterisitcs of the corresponding diamond electrodes, which can be observed by cyclic voltammetry and electrochemical impedance spectroscopy measurements. These two measurement techniques play an important role in the characterization of the diamond electrodes and are therefore discussed in detail. One important parameter which is investigated is the electronic surface barrier of diamond in contact to the electrolyte, which can vary over a range from below 1.0 eV to almost 2.0 eV depending on the oxidation treatment.
Apart from the oxidation treatments, the cases of single-crystal and nanocrystalline diamond are compared. It is shown that the grain boundary network can also affect the characterisitcs of diamond electrodes.