Chapter 1

Introduction

Diamond has attracted much attention due to its promising electrical, mechanical, and electrochemical properties. The wide bandgap of approx. 5.4 eV, the high electrical breakdown field, the high saturation velocities for holes and electrons and the high thermal conductivity are expected to enable the use of diamond for electronic devices for high power- and high temperature applications which cannot be realized with silicon-based MOS devices. Another promising field of application are micro-electro-mechanical systems (MEMS) like switches or mechanical sensors, since diamond has also attractive mechanical properties like a high Young´s modulus or a high fracture strength.

In addition, diamond is exceptionally chemically stable, which makes it an ideal material for electrochemical applications in harsh environments, like waste water treatments or electrochemical sensing in a wide range of pH. Other important electrochemical characteristics of diamond are the wide potential window of water dissociation and the extremely low background current. Besides, diamond is a biocompatible and optically transparent material. This is essential for the analysis of biochemical processes with simultaneous fluorescence measurements.

However, the electrochemical properties of diamond are strongly dependent on the surface termination and are therefore sensitive to surface treatments. One common example is the oxidation of the hydrogen-terminated diamond surface, e.g. by chemical or plasma treatments. For applications under strong oxidizing conditions, oxygen-terminated diamond is therefore the standard material. However, there is a variety of different carbon-oxygen functional groups with different bond strengths possible on the diamond surface. Therefore, the electronic and electrochemical properties of diamond oxidized by different surface treatments might not be the same. To optimize the characteristics of diamond for electro- or biochemical applications, it is therefore necessary to analyze and understand the effect of different surface treatments on the electrochemical properties of diamond.

Another important point is that poly- or nanocrystalline diamond is used for many practical applications, since the growth of single-crystal diamond is currently limited to relatively small samples. The characteristics of nanocrystalline diamond might differ from those of single-crystal diamond due to the grain boundary network, which might have sp^2-like characteristics.

This work describes the characterization of oxygen-terminated boron-doped diamond for electrochemical applications. The work is focussed on the effect of different surface oxidation treatments on the electrochemical and electronic properties like the electronic surface barrier in contact with an electrolyte, the potential window of water dissociation, the background current, and the oxygen evolution characteristics. The characterization will be performed for single-crystal and nanocrystalline diamond electrodes.

After an introduction summarizing the electrochemical properties of diamond (chapter 2), the growth of diamond films by chemical vapor deposition will be shortly described in chapter 3. In chapter 4, the electrochemical measurement methods used for the characterization of the diamond electrodes will be explained. This analysis is another important point of this work. This chapter also contains an introduction into the characteristics of a semiconductor-electrolyte interface. In chapter 5, the oxidation of diamond by wet-chemical, electrochemical and plasma treatments will be explained. It will be shown by X-ray photoemission spectroscopy (XPS) that these oxidation treatments induce different carbon-oxygen groups on the diamond surface as well as different amounts of sp^2-content. The effect of these surface treatments on the electrochemical characteristics of diamond electrodes will be shown in chapter 6, which is one of the main parts of this work.

In chapter 7, possible applications of diamond in electrochemistry are shown. This chapter describes the use of diamond electrodes for the oxidation of ethanol, the fabrication of sub-microelectrode arrays realized completely in diamond and nanocrystalline diamond electrodes with Au nanoparticles. In this chapter, it will be also shown that the analysis used for the characterization of the diamond electrodes in chapter 6 can also resolve the heterogeneous characteristics of the microelectrode arrays or the electrodes decorated with metal particles.

As a comparison to diamond, the electrochemical properties of gallium nitride and indium nitride electrodes will be discussed in chapter 8. It will be shown that these electrodes are not stable under harsh anodic conditions, although III-nitride semiconductors are usually considered to be chemically inert. The stability against anodic oxidation is therefore one main advantage of diamond electrodes.

Chapter 2

Diamond for Electrochemical Sensing

2.1 Electrochemical properties of diamond

Apart from the exceptional electronic and mechanical properties like high electron and hole mobility (for intrinsic material), high electronic breakdown voltage, high mechanical fracture strength and high Young´s modulus [1, 2, 3, 4], diamond is also a very attractive material for electro- and biochemical applications [5]. Diamond is chemically inert and in the case of oxygen termination stable even under harsh oxidizing conditions, e.g. under anodic polarization or in oxidizing acids. Besides, the stability of diamond is not limited to aqueous electrolytes. As an example, it has been shown that diamond electrodes can be used in very corrosive molten alkali chloride electrolytes [6].

Another important property which makes diamond interesting for electrochemical applications is its wide potential window of water dissociation with extremely low background currents compared to widely used metal electrodes like platinum or gold. Fig. 2.1 shows typical cyclic voltammetry measurements (which display the current across the electrode-electrolyte interface in dependence on the electrode potential) of a high-quality diamond and a platinum electrode. The potential window is limited by the hydrogen evolution reaction at negative (cathodic) potentials and the oxygen evolution reaction at positive (anodic) potentials. For platinum and other metals, the potential window is close to 1.23 V, which is the difference between the equilibrium potentials of both reactions [7]. For diamond, the potential window is typically in the range of 3.0 - 3.5 V, as it will be also shown later. The wide potential window of diamond in aqueous electrolytes is usually ascribed to the weak interaction of the diamond surface with molecules from the electrolyte. Therefore, reactions which require the adsorption of dissolved species are shifted to higher potentials [5, 8]. E.g., the hydrogen evolution reaction on hydrogen-terminated diamond can be described by the Volmer-Heyrovsky mech-

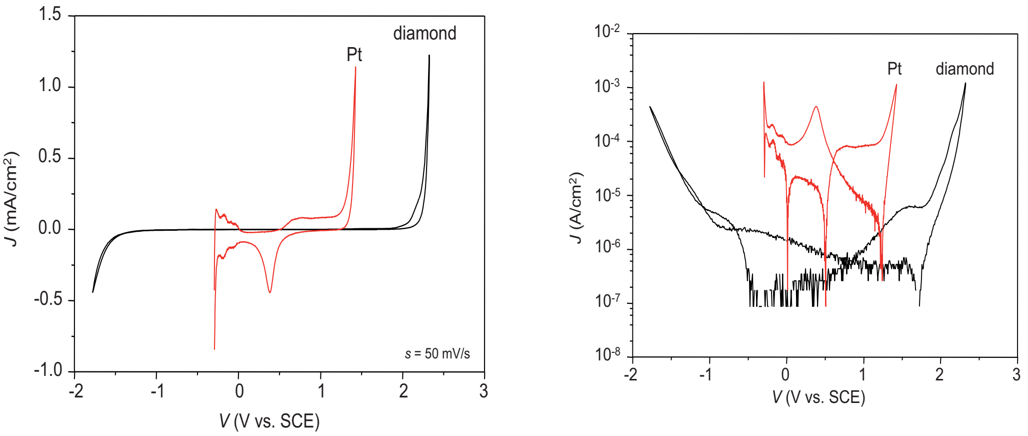


Figure 2.1: Typical cyclic voltammetry measurements of diamond and platinum in 0.1 M H_2SO_4. (a) linear scale, (b) semilogarithmic scale

anism [8, 9, 10], where a hydronium ion is discharged at a hydrogen site on the diamond surface:

$$C - H + H_3O^+ + e^- \rightarrow C\bullet + H_2 + H_2O \tag{2.1}$$

This is the rate-determining step of the hydrogen evolution reaction. The diamond surface is then regenerated by the adsorption of another hydronium ion:

$$C\bullet + H_3O^+ + e^- \rightarrow C - H + H_2O \tag{2.2}$$

In these equations, C• depicts a reactive site on the diamond surface.
However, the diamond electrodes which are analyzed in this work are oxygen- and not hydrogen-terminated. It might be that the reaction proceeds again according to the Volmer-Heyrovski-mechanism, where the adsorption of the hydronium ions takes place at a C-OH or C=O site. Such a reaction mechanism has been proposed for metal oxide electrodes [11]. However, there are no detailed studies about the hydrogen evolution on oxygen-terminated diamond electrodes yet.
The mechanism of the oxygen evolution reaction on diamond proceeds most probably via several parallel reactions paths, which is the case even for metal electrodes [12]. Therefore, a detailed investigation is nearly impossible.
The wide potential window of diamond might enable the detection of charge-transfer reactions at high cathodic or anodic potentials outside the potential window of metal electrodes. However, this will be only the case for simple charge-transfer reactions which do not require a strong interaction of ions with the diamond surface, like the adsorption of reactants or intermediate products. Otherwise, also these reactions will be shifted to higher anodic potentials.

Another contribution to the *measured* potential window of diamond electrodes can be also the depletion layer close to the surface, which leads to an additional potential drop across the diamond. This is the case especially for low-doped electrodes.

The low background current, which is mainly determined by charging and decharging of the electrode interface, enables the detection of very small signals, which is important e.g. for biochemical measurements, where signals in the pA-range have to be resolved.

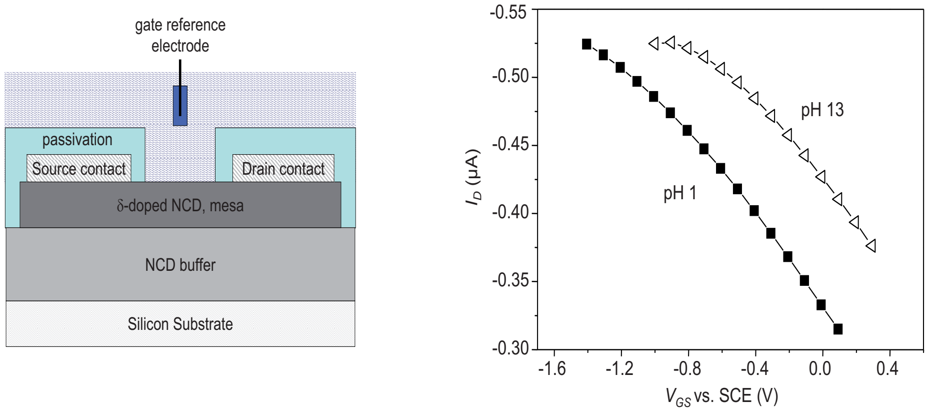
However, the potential window and the background current of diamond electrodes are very sensitive to the material quality. Low-quality diamond electrodes can contain a high amount of non-diamond (sp^2) contaminations. This leads to a decreased potential window and to higher background currents. In this case, the electrodes can be similar to glassy-carbon or graphite electrodes [5, 13, 14]. A similar effect has an extremely high boron doping concentration ($N_A \approx 5\times10^{21}$ cm^{-3} or more), which can lead to the formation of boron carbide clusters. Therefore, an optimization of the growth conditions is essential for the fabrication of diamond electrodes.

2.2 Diamond electrodes and ISFETs

The electrochemical applications of diamond can be divided into amperometric and potentiometric sensors. Amperometric sensors record a current across the diamond-electrolyte interface, which is related to the oxidation or reduction of the ions or molecules to be detected and therefore dependent on the concentration of this substance in the electrolyte. On the other hand, potentiometric sensors are based on the change of the surface potential in dependence on the electrolyte composition, e.g. the pH-value.

One example for amperometric sensing is the oxidation of organic compounds on diamond electrodes, which can be used for their detection. Examples are the detection of phenol [15, 16], carboxyl acids [17], ethanol, or other substances [18, 19]. As an example, the detection of ethanol on diamond electrodes will be shown in chapter 7. Besides, the anodic oxidation of such substances can be used for waste water treatment [16, 20], since the organic and maybe toxic compounds can be converted to non-toxic compounds. The stability of the diamond electrodes under high anodic potentials is an important condition for these applications.

Another widely studied application is the use of diamond for ion-sensitive FET (ISFET) structures, mainly for pH sensing. Such a device operates in the potentiometric mode, where the change in the surface potential due to the pH results in a change of the drain-source current of the ISFET. There are mainly three concepts for a pH sensor based on diamond: The most common one is the use of a partially hydrogen- and partially oxygen-terminated surface, where the hydrogen-



(a) (b)

Figure 2.2: (a) scheme of an oxygen-terminated diamond ISFET with boron δ-doped channel, (b) transfer characteristics in pH $=$ 1 and pH $=$ 13 [23]

terminated areas induce the conducting channel and the oxygen-terminated areas the pH sensitivity [21]. A similar approach is the use of a partially aminated surface [22]. However, such devices suffer from instability, since the hydrogen termination can be converted to oxygen termination under anodic conditions, leading to a decrease of the channel conductivity. Therefore, the operation of such devices is limited to small drain-source and gate-source voltages and to non-oxidizing electrolytes. A better stability can be achieved using completely oxygen-terminated ISFET structures with boron-δ-doped channels [23, 24]. Such an ISFET structure on oxygen-terminated nanocrystalline diamond is shown in fig. 2.2(a). The drain-source current of a FET structure can be modulated by a gate voltage applied to a reference gate electrode which is immersed into the electrolyte. The pH sensitivity of the diamond surface results in a shift of the transfer characteristics with up to 59.2 mV/pH (fig. 2.2(b)).

The disadvantages of such FET structures are currently relative low current levels and a limited modulation of the channel. A third possibility is therefore the combination of an oxygen-terminated diamond electrode with a FET structure based on another material with better electronic properties, e.g. AlInN/GaN heterostructures [25].

Another field of growing interest is the use of diamond for biological applications, like attaching of DNA strands or proteins to the diamond surface [26, 27, 28], or cell measurements with patch-clamping systems [29] or quadrupole structures. Biochemical measurements can be done using electrode or FET structures. For such applications it is important that diamond is bio-compatible and optically transparent. Here it has to be noted that the optical transparancy is reduced by boron doping. However, the transparancy of the complete sample including a transparent substrate, an intrinsic buffer layer and a boron-doped active layer is not significantly reduced as long as the thickness of the doped layer is in the range of a few hundred nanometers or below [30]. This promises to allow simultaneous electrochemical and fluorescence measurements. An attractive approach for this application is the growth of nanocrystalline diamond on optically transparent glass or sapphire substrates [30, 31, 32].