Influence of ambient humidity on the surface conductivity of hydrogenated diamond

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Abstract

The enhancement of the electrical conductivity of hydrogen-terminated diamond surfaces due to the adsorption of various chemical species represents a challenging problem and has a high application potential as well. In the transfer doping model of Maier et al. the presence of a water layer that forms spontaneously in moist atmospheres on any surface plays a crucial role. Hence, in the present contribution we have focused our attention on the influence of the relative humidity (RH) on the surface conductivity. In order to perform conductivity measurements in a wet atmosphere an original technique eliminating leakage effects due to adsorbed water was developed. The conductivity was measured at room temperature for RH between 2% and 100%. Despite a rather weak dependence on RH, three well distinguished regions can be identified in the conductivity as a function of RH. Not pretending to offer a first-principles account for this behaviour, a phenomenological explanation of the data is given.
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1. Introduction

The unexpectedly high conductance (typically $\sigma^{\square} \approx 10^{-5}$ S per sheet at room temperature) of hydrogen-terminated surface of diamond discovered in 1989 by Landstrass and Ravi [1] is a phenomenon interesting enough theoretically, with promising applications as well. It is believed that the effect itself is due to the existence of a relatively stable hydrogen termination of the diamond surface persisting up to 700 °C, the properties of which do not depend on a particular technique used for its preparation (CVD epitaxy, thermal hydrogenation). On the other side, as far as it is known a similar enhancement of conductance is not observed on diamond surfaces treated in another way, e.g. on oxidized surfaces. The hydrogen termination is, however, necessary but not a sufficient condition for the existence of the effect. As was reported later [2,3] for already hydrogenated diamond surface an increase of its conductance takes place only if it is in contact with the surrounding atmosphere. It is assumed that the chemisorbed water dissociated under the influence of gaseous atmospheric species (e.g. CO_2) and surface forces may act as an acceptor which depletes

electrons from the bulk of the diamond crystal and creates a conductive p-type channel just below its surface. Essential features of such a mechanism can be accounted for by an electrochemical model of the so called *transfer doping* as proposed by Maier et al. [3]. Accordingly, the presence of H–C double layer on the surface of diamond changes the alignment of energy levels in the system in such a way that the electrons from the diamond are injected into a thin water film spontaneously formed on the free surface exposed to the atmosphere. Such a film being, as a rule, acidic [2,4] serves then as an efficient acceptor keeping electrons apart from the conductive hole channel in diamond. As has been observed recently, also fullerens [5] and fluorofullerens [4] may serve as such acceptors inducing in hydrogenated diamond a similar enhancement of surface conductivity as the natural water film. Electrochemical transfer doping model accounts nicely for the observed orders of magnitude decrease of surface conductance evoked by the vacuum thermal annealing performed in the range well below the critical temperature of hydrogen termination ($\sim$ 700 °C) and, simultaneously, it is apt to explain rather a high absolute value of the sheet conductance ($\sim 10^{-5}$ S) which is quite uncommon for smooth (non-porous) insulators [6] where the surface conductance ($< 10^{-12}$ S at room temperature and $\sim$ 90% relative humidity) is traditionally connected with the electrochemical transport via the

thin adsorbed water film. It should be stressed, however, that the understanding of the complex processes taking place on the hydrogen-terminated diamond surface exposed to the open air is far from being perfect and, consequently, a more detailed research into the particular problems is required.

Therefore, in the present work we have turned our attention to a somewhat marginal but practically important problem, the investigation of the influence of the ambient partial pressure of water, measured in terms of relative humidity (RH), on the surface electric conductance of the hydrogenated diamond.

2. Experimental

For our experiments we have used an artificial, intently undoped, HTHP-grown single crystal diamond of dimensions of $\sim 5 \times 5 \times 1$ mm, which was thermally hydrogenated in an atmosphere of purified H_2. The detailed description of the apparatus and the process of hydrogenation may be found in our previous studies on this subject [7]. After the hydrogenation, the contacts were evaporated (as detailed below) and the samples were kept at room temperature and ambient humidity for a week, till the measurement of conductivity at variable ambient humidity was carried out.

By studying the humidity dependence of conductivity of the hydrogenated diamond surface, we have met problems of rather a special kind. One class of the problems is closely related to topology of the as-prepared hydrogenated surface and the realization of low-noise contacts, while the other to the existence of large leakage currents disturbing the electric measurements in a wet atmosphere. An increased attention has been also paid to rather an uncommon method for long-term control of relative humidity by means of aqueous solution of sulphuric acid. As these techniques are either new or less known, we have found it necessary to give to their description more space than it is usual in a standard research paper.

A van der Pauw technique [8] traditionally used for the evaluation of the sheet conductivity of arbitrarily shaped thin layers cannot be, unfortunately, used in our case without serious objections. The application of this method requires, namely, that the flat arbitrarily shaped sample is single-connected and provided with four-point contacts placed just on its circumference. The as-prepared hydrogenated layer on the diamond surface has, however, rather the topology of a spherical shell and therefore without an additional shaping the van der Pauw method cannot be applied. Moreover, as was shown by preliminary experiments the point contacts prepared by a technique which does not likely change the hydrogen coverage, i.e. vacuum evaporation of gold, were found to have a large noise. In order to avoid masking of the sample during high temperature hydrogenation or, alternatively, an additional shaping of the active area and an optimization of point contacts (notice that all of these procedures may appreciably change the properties of the surface layer under investigation!) the following original technique was developed.

The main idea of the method is to use, instead of point contacts, large perimeter contacts the noise of which is, as a rule, small, even if their quality is inferior and, simultaneously, to provide measures for the elimination of leakage currents inevitably appearing in the wet ambient. The realization of these tasks is theoretically based on an application of somewhat curious, less known theorem of electrostatics, namely, Lampard–Thompson's theorem [9], utilized in metrology for the construction of a calculable normal capacitor and that is why we call this technique tentatively "Lampard's method". The above mentioned theorem may be formulated as follows (see inset in Fig. 1). Let a cylindrical conducting shell with a plane of symmetry, but otherwise arbitrary be divided into four insulated parts by the said plane of symmetry and any plane perpendicular to it. Then the vacuum capacitance measured between opposite sections, A and C, of the cylinder (i.e. so called cross capacitance) is given by:

$$C_0 = L\varepsilon_0 \ln 2/\pi = L \times 1.953549...\,\mathrm{pF}, \tag{1}$$

where L is the length of the cylinder (SI units are used throughout the paper). By the cross capacitance measurement the testing potential is applied to one electrode only while the opposite and two other electrodes are kept at zero potential. Filling the system with a dielectric of resistivity ρ and relative permittivity ε, we can write an expression for Maxwell's relaxation time in the form $\rho\varepsilon\varepsilon_0 = R\varepsilon C_0$ enabling one to determine the resistance R, which should appear between the same electrodes as the cross capacitance (cf. [10]). Taking into account the fact that the corresponding electrostatic problem is essentially two-dimensional, we can rewrite the resulting formula also in terms of sheet resistance $\rho^\square$ ($\rho^\square = \rho/L$) as

$$R = \rho^\square \pi / \ln 2. \tag{2}$$

A simple design of the electrode system convenient for sheet resistance measurements of thin layers respecting the conditions required by Lampard–Thompson's theorem is depicted in Fig. 1 together with the necessary circuitry. The side electrodes B and
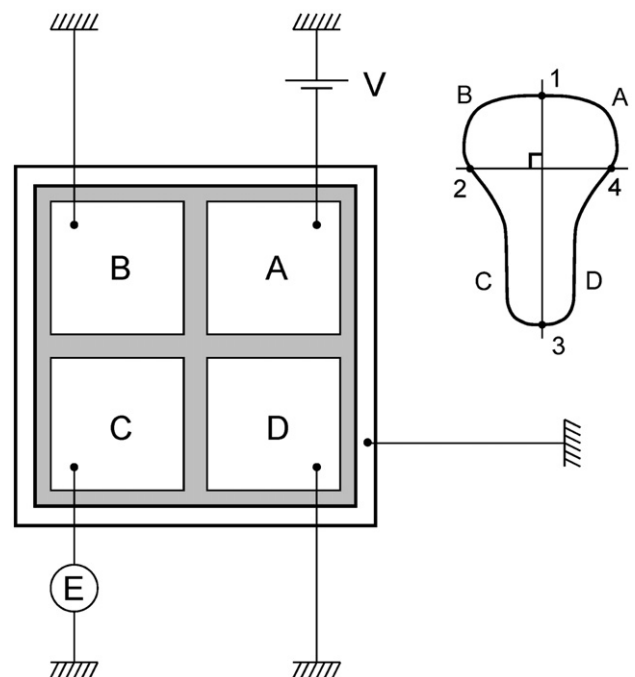

Fig. 1. Schematic view of sample configuration and circuitry as used in the experiment. Inset: illustration to Lampard–Thompson's theorem.