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Growth, Preparation and Surface Modification of Microcrystalline Diamond Powder for the Synthesis of Diamond Ceramics

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Abstract

Chemically modified microcrystalline diamond surfaces have been prepared and investigated on the basis of thermodesorption measurements, X-ray diffraction and X-ray photoemission spectroscopy. X-ray investigations and SEM-images show that the synthesized diamond powder consists of pure carbon crystals of cubic modification with unbroken facets. Investigation of acidic functional groups, having different oxygen content and bound on the diamond surface by an oxidizing process, was carried out by the method of neutralization with different alkaline reagents. It has been shown that the concentration of the groups neutralized by each reagent decreases as the temperature of the heat treatment during preparation is raised. Under thermal treatment, the oxy- functional groups decompose at T>*600°C, leaving a hydrogen terminated diamond surface. Hydrogen desorbs at* T>*1000°C, thus generating an atomically clean surface, such as is required for direct bonding of the nano- and microcrystals during sintering.*

Gegenstand der vorliegenden Veröffentlichung ist die Synthese von Diamantpuder, sowie dessen chemische Reinigung und Modifikation der Oberfläche. Chemisch modifizierte mikrokristalline Diamantoberflächen wurden präpariert und auf der Basis von Thermodesorptionsmessungen, Röntgenbeugung und Röntgen-Photoemissionsspektroskopie untersucht. Die Röntgenuntersuchungen und rasterelektronenmikroskopische Aufnahmen zeigen, daß die synthetisierten Puder aus reinen Kohlenstoffkristallen kubischer Modifikation mit ungebrochenen Facetten bestehen. Mit Hilfe der Neutralisationsmethode wurde das Verhalten saurer funktionaler Gruppen mit unterschiedlichem Sauerstoffgehalt, die durch einen Oxidationsprozeß an der Diamantoberfläche gebunden wurden, unter Verwendung unterschiedlicher alkalischer Reagenzien untersucht. Es wurde gezeigt, daß die Konzentration der Gruppen für jede der verwendeten alkalischen Reagenzien mit zunehmender Temperatur bei der Wärmebehandlung abnimmt. Durch die Wärmebehandlung zersetzen sich die funktionalen Gruppen bei T>*600°C und hinterlassen eine mit Wasserstoff terminierte Oberfläche. Der Wasserstoff desorbiert bei* T>*1000°C and erzeugt so eine atomar reine Oberfläche, die für die direkte chemische Bindung der Nano- und Mikrokristalle beim Sintern erforderlich ist.*

Introduction

Due to its extreme physical properties, diamond is an attractive material for a broad range of applications that include high power, high temperature electronics and optical and superhard mechanical components.

Use of natural or synthetic diamond has already resulted in considerable progress towards the fabrication of discrete electronic devices.[1] High materials cost and device integration problems, however, limit single crystalline bulk diamond to very selected applications. A possible alternative, for some applications, is presented by polycrystalline diamond films[2] already employed as heat spreaders for the effective operation of high power semiconducter lasers. These films, made by chemical vapor deposition (CVD) posess a unique structure that is polycrystalline in nature but with some degree of orientation. However, these films are more expensive than such optical materials as zinc selenide and sapphire and have a very limited application. Because the production of diamond powder is already a relatively cheap high volume technology, the fabrication of bulk diamond ceramics may became an attractive solution to the problem. However, there are a number of technological difficulties to overcome. Surface graphitization of the microcrystals during sintering is one example. In this work, the surface properties of chemically modified microcrystalline diamonds have been investigated. The surface phenomena, which are determined by the composition, structure and reactivity of the functional groups on the diamond surface are of great interest for the synthesis of diamond ceramics. Various functional groups have been added to the crystallite surface to minimize, and possibly avoid graphitization at the surface during the ceramic sintering process. The surface condition critically affects interfacial bonding between adjacent grains and, hence, the mechanical properties of the ceramic material itself.

There are several reasons for the uncommon occurrence of diamond:[3,4]

- the entropy of diamond is less than the entropy of graphite by 0·78 cal/Kmol;
- a large activation energy barrier exists between graphite and diamond, which prevents even small particles from forming at room temperature under equilibrium conditions. The density of diamond (3·51 g/cm^3) is significantly higher than that of graphite. Therefore the former becomes the equilibrium form of carbon only at high pressure.

These facts certainly also apply to the formation of the nano- and microcrystalline diamonds used in this study.

Figure 1 displays the phase diagram of carbon, summarizing the different experimental routes for diamond synthesis, and the phase separating lines, a, b, c.

Although diamond would be the stable phase at room temperature at a pressure of 2 GPa, it does not form under these conditions, primarily due to the extremely low kinetics of the process. Bulk diamond grows from graphite only when the temperature increases to at least several hundred degrees, or in the presence of a catalyst like molten nickel or manganese, with $P>6$ GPa and $T>1200°C$. The difficulties of diamond formation are largely due to the high thermodynamic stability of the graphitic planes, melting above 4000 K.[5] Thus the transformation from the planar sp^2-structure to the three-dimensional sp^3-network accounts for the required high temperature and pressure.

Experimental

In this work, microcrystalline diamond has been synthesized from doped graphite, employing the spontaneous crystallization method under high static pressure corresponding to zone 1 of Fig. 1. Crystal growth was carried out in an apparatus of the anvil type. Growth conditions were as follows: pressure 4·5 GPa, temperature 1200°C. The Mn–Ni system has been used as the catalytic agent. The catalyst dissolves carbon from the graphitic phase, which then precipitates the 'allotropic' stable phase under equilibrium conditions, where diamond is formed. A defined size of the diamond particles can be achieved by controlling the duration of the process, usually around 2 min. Subsequently, the samples have been purified and classified by their grain size. Impurities from the metallic catalyst and graphitic fragments have been removed in a boiling acidic solution of H_2SO_4+ CrO_3.The surface of the microcrystals finally has been purified by boiling in a concentrated $HClO_4$ solution, which also forms the highly reactive oxygen groups on the surface of the microcrystals.

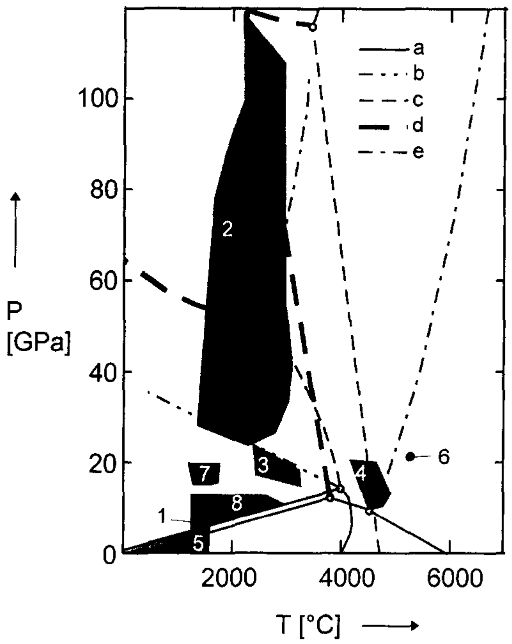

Fig. 1. P-T phase diagram of carbon. Experimental methods of diamond synthesis: (1) Statical method. (2) Dynamical method. (3) The method of the graphite–diamond direct junction at the statical conditions. (4) High-temperature synthesis using the detonation wave. (5) Epitaxial method. (6) The melt-solution method (from graphite). (7) Graphite Longsdailit direct junction at the statical conditions. (8) Direct synthesis from the elementary carbon and organical combinations. Phase separating lines: (a) Graphite–diamond, graphite–liquid. (b) Metastable graphite. (c) Diamond–liquid. (d) Diamond – metallic carbon. (e) Metallic carbon–liquid.

Diamond has a very high surface energy resulting in modified bonding properties upon exposure to chemically reactive species. To minimize the surface free energy, so-called functional groups are formed on the surface, which are strongly bonded to the outer carbon surface atoms. The removal (disposal) of the oxy-functional groups obtained is feasible at relatively high temperatures only. The products of their decay should be in this case CO and CO_2 that means the graphitization of the diamond surface. Boehm and Suppok show[6,7] that the concentration of the oxy-functional groups is strongly dependent on the oxidizing temperature (by using gas-phase oxidation) and oxidizing reagent (by chemical treatment). Oxygen gives rise to different oxy-functional groups (see Fig. 2(b)) which affect the chemical activity of the diamond surface differently. Because of this, there is opportunity to control the colloid-chemical properties of the diamond by the modification of the oxy-functional groups. The formation of the different oxy-functional groups and their modification by temperature treatment was investigated in the present work. As outlined above, oxidation of the crystals in concentrated $HClO_4$ solution is the final preparation step of the diamond powder, resulting in the formation of oxy-functional groups on the surface. According to the standard modern chemical structural model diamond consists of the skeleton and surface functional groups (see Fig. 2(a) and 2(b) respectively). The application of alkali neutralization to the oxy-functional groups on the diamond surface after boiling in $HClO_4$ solution shows an acidic reaction. Consequently the bonding of definite functional groups by oxidizing reactions has been investigated in order to find a method to adjust the surface conditions of the crystallites. As object under study, natural and synthesized diamond powder with crystallite sizes up to 14 μm were considered. The oxidizing process of the diamond samples was established in the boiling $HClO_4$ solutions or from the gas phase using oxygen. Duration of the boiling in acid was 2 h. The concentration of the oxy-functional groups on the diamond surfaces has been determined via the titration method by neutralization with $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ in a 0.05 mol solution. The specific surface area of the material ranges from 30 m^2/g to 1 m^2/g.

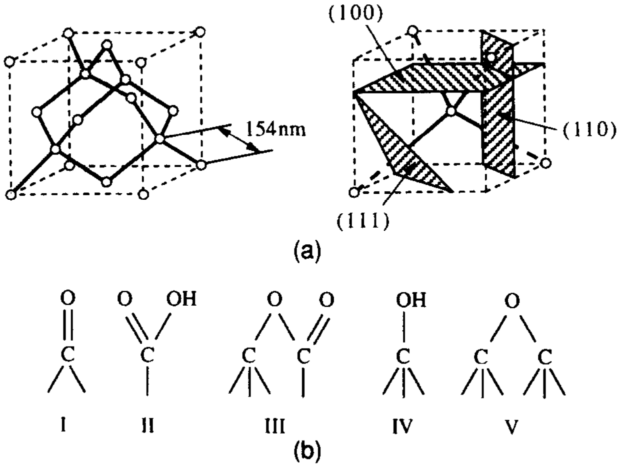

Fig. 2. (a) Structure of diamond skeleton. (b) Surface of diamond, functional groups: I carbonyl; II carboxyl; III lactonic; IV tertiary alcohol; V ether groups.

Results and Discussion

Figure 3 displays a scanning electron microscopic (SEM) image of the microcystalline material under study. The size of the crystals ranges from below 1 to 14 μm and crystal surfaces are undistorted.

The crystallographic properties of the synthesized diamond samples were investigated by X-ray diffraction (XRD). Figure 4 shows the X-ray diffraction pattern of the powder. CoKα-radiation has been used for excitation. The pattern shows the typical diamond structure. No other, i.e. graphitic modification has been observed. The concentration of the different functional groups bound on the diamond surface due to the oxidizing process was investigated and is shown in Table 1. The selective neutralization of these groups, having different oxygen contents, was carried out by the use of $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ 0.05 mol solutions. Neutralization through the $NaHCO_3$ solution occurs due to the presence of the strong acidic carboxyl group, as indicated in Fig. 2(b), case II. For $NaOC_2H_5$, neutralization at the surface occurs due to both the strong acidic groups and the weak hydroxyl groups, as indicated in Fig. 2(b), case IV. Na_2CO_3 and NaOH account for another type of neutralization than the strong or weak acidic groups. With increasing temperature during sample treatment (boiling in the acids or oxidizing in dry oxygen atmosphere at T=100–570°C) the amount of neutralized functional groups decreases, as indicated in Table 1. To estimate the concentration and structure of the functional groups, thermodesorption and X-ray photoelectron spectroscopy of the crystals have been used.

Thermodesorption experiments have been performed under He-flow at a pressure of 0·1–0·15 MPa at a flow rate of 0·4–0·6 cm^3/s by slow ramping up of the temperature. Thermodesorption spectra are displayed in Fig. 5. Typically, CO and CO_2 from the thermally decomposing oxy-functional groups desorb at a temperature of 500–600°C. This leaves a hydrogen terminated diamond surface in this range of temperature. Desorption of hydrogen from the surface is observed at a temperature of 1000°C, generating finally an atomically clean diamond surface. The thermal decomposition of the oxy-functional groups is described by the following reactions:

$$C(OH) \rightarrow C(H) + CO \text{ and } C(OOH) \rightarrow C(H) + CO_2;$$

and results in the emission of CO and CO_2, respectively and hydrogenation of the surface.

The data in Fig. 5 also indicate that oxidation in hot $HClO_4$ solution is more effective than

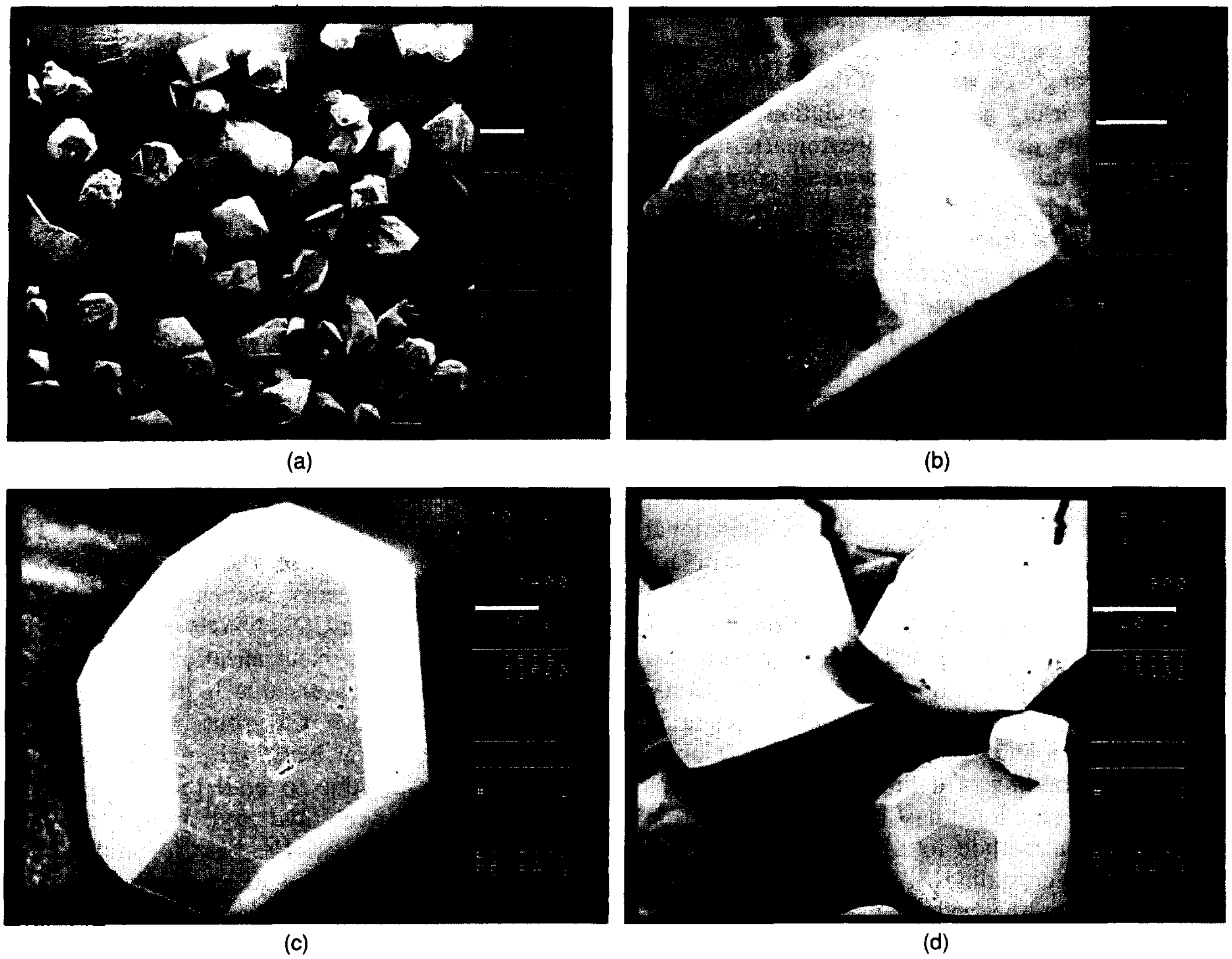
(a) (b) (c) (d)

Fig. 3. SEM image of the diamond powder.

oxidation in a dry oxygen atmosphere at T=400°C. For the estimation of the desorption energy E of CO and CO_2 the approximation of the maximum in the linear program-simulated thermodesorption spectrum was used. Taking into account the approximation restrictions[8] the energy of the activation reactions of thermodesorption from the diamond surface is found as following: E_{CO_2}=230–260 kJ/mol and E_{CO}=230–290 kJ/mol.

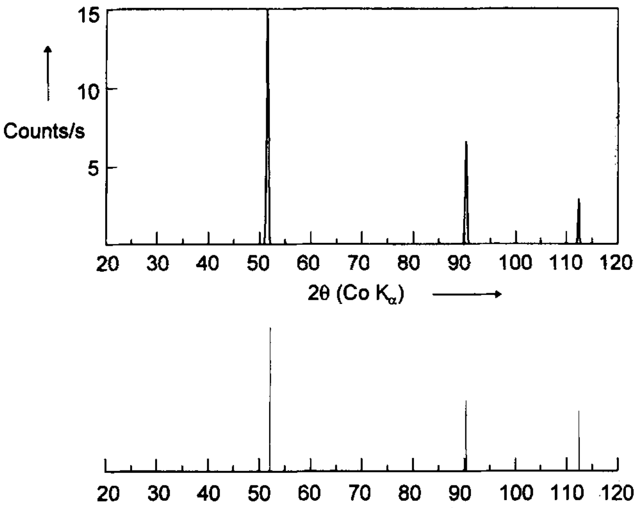

Fig. 4. XRD spectrum of the diamond powder (CoKα).

The findings from the thermodesorption experiments are corroborated by X-ray photoemission spectroscopy (XPS) with the resulting spectra shown in Fig. 6. This surface sensitive method provides information on the chemical bonding state, degree of coverage and chemical composition.

Data have been recorded with the ESCALAB-5 installation, using AlKα- radiation for photoelectron excitation and the constant energy mode of the energy analyzer.

The complete spectra (not shown) reveal an impurity level at the diamond surface of approximately 1 at% or less. Figure 6, finally, shows the oxygen 1s XPS-peak, centered at a binding energy of 531·6 eV, upon exposure of the diamond crystal to treatment in $HClO_4$ solution. For comparison, also the spectrum upon treatment in He-atmosphere at 800°C is shown. The acidic treatment of the diamond surfaces results in a very broad O1s-peak, extending up to a binding energy of 537 eV. The unusual broadening is attributed to the presence of various species of the oxy-functional

Table 1. Concentration of oxy-functional groups on the diamond surfaces after oxidation, determined using different alkaline reagents for neutralization

Temperature of sample treatment (°C)	*Concentration of oxy-functional groups (mg-equiv/m^2)*			
	$NaHCO_3$	*Na_2CO_3*	*NaOH*	*$NaOC_2H_5$*
100	2·27	2·94	4·42	4·75
220	1·56	2·08	3·59	3·81
350	0·91	1·25	2·34	2·62
570	0·1	0·21	0·45	0·55

groups on the surface, as illustrated in Fig. 2. Not shown is the carbon 1*s*-peak, since only a very small chemical shift has been observed. Taking into account the total peak area of the carbon and oxygen 1*s*-levels and normalization to the respective photo-ionization cross-sections, the concentration ratio between oxygen and carbon is estimated to be 0·1.

For estimation following equation was used:
$C_O/C_C = [T(O1s)\ \sigma(C1s)]/[T(C1s)\ \sigma(O1s)]$;
where:
C_O — oxygen atoms concentration;
C_C — carbon atoms concentration;
T — total area peak;
σ — photo-ionization cross-section of electronic level.
$\sigma(C1s)/\sigma(O1s) = 0{\cdot}36$ then yields $[C_O]/[C_C] = 0{\cdot}10$.

The ratio $[C_O]/[C_C] = 0{\cdot}1$ corresponds to one monolayer coverage of the surface (approximately one atom of oxygen per one atom of carbon).

These data are in a good agreement with the thermodesorption data.

Concluding Remarks

The formation of nanosized diamond powders by the statical method under the conditions mentioned above is satisfactorily stable. The result of the interaction between the atomically-clean diamond surface and the low-molecular compounds is the formation of functional groups. The removal of the oxy-functional groups obtained is possible only at high temperatures. Because the products of their decay should be CO and CO_2 the decay could be accompanied by the destruction of the diamond skeleton too. The reactivity of the surface functional groups is especially important for the synthesis of diamond ceramics. Consequently the bonding of definite functional groups by oxidizing reactions has been investigated in order to find a method to adjust the surface conditions of the crystallites. It was shown that the formation process of the oxy-functional groups was strongly dependent on the oxidizing reagent and was a function of temperature. As the temperature during treatment rises the concentration of the diamond oxy-functional groups neutralized by each investigated reagent decreased. The highest density of free bonds of the diamond surface was demonstrated for the $HClO_4$ treatment. The XPS investigations show the ratio $[C_O]/[(C_C]=0.10$, which corresponds to one monolayer coverage of the diamond surface. The energy of the activation reactions of thermodesorption from the diamond was found as following: E_{CO_2}= 230–260 kJ/mol and E_{CO}= 230–290 kJ/mol.

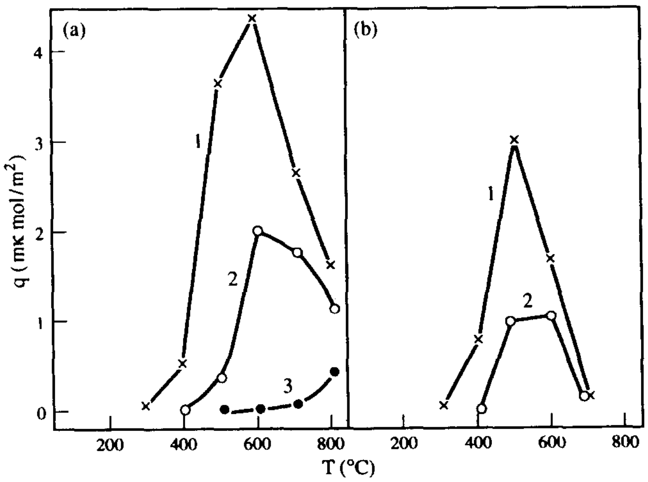

Fig. 5. Thermodesorption spectra of diamond powder CO (a) and CO_2 (b). (1) Sample after oxidizing in $HClO_4$. (2) Sample after oxidizing in O_2 atmosphere at T=400°C, duration 30 min. (3) Treatment in He, at T=800°C, then in environmental atmosphere at T=20°C.

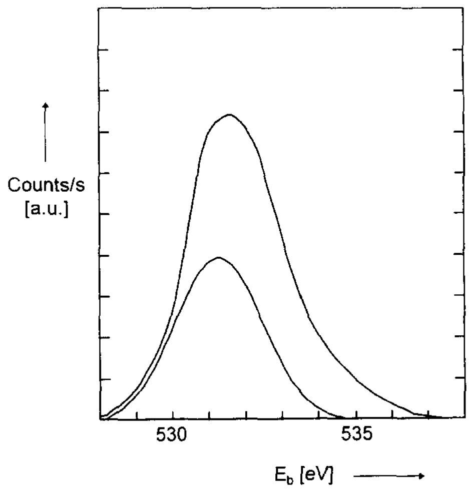

Fig. 6. XPS spectra of diamond surface: (a) C1*s*, (b) O1*s*. (1) after treatment in $HClO_4$. (2) after treatment in He atmosphere at T=800°C.

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