

# Incorporation of butyl groups into chlorinated diamond surface carbons by organic reactions at ambient temperature

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Hydrogenated diamond powder has been chlorinated by a radical reaction using sulfur chloride in chloroform at 50 °C. The chlorinated diamond was then treated with *n*-, *sec*- and *tert*-butyllithium in tetrahydrofuran at 30 °C for 4 h, and butyl groups were incorporated onto the surface. The modified diamond powder was characterized by diffuse reflectance IR Fourier-transformed (DRIFT) spectroscopy. The surface substituents were decomposed by flash pyrolysis in a nitrogen flow at temperatures between 255 and 1040 °C and essentially all organic fragments were recovered. When the pyrolysis temperature was increased, the total amount of recovered carbons gradually approached a constant value. The fraction of butylated surface carbons to the total surface carbons was calculated based on pyrolysis products obtained at 1040 °C and was 0.055 for *n*-butylation, 0.040 for *sec*-butylation and 0.047 for *tert*-butylation.

## 1 Introduction

The outstanding properties of diamond and recent developments in its gas-phase synthesis indicate that it holds considerable promise for use in fields of tribology and electronics.<sup>1</sup> When diamond is synthesized by chemical vapour deposition (CVD), CH<sub>4</sub> and H<sub>2</sub> are typically used as the starting materials. Since the bonding energy of a C–Cl bond is less than that of a C–H bond,<sup>2,3</sup> however, reactants of carbon–hydrogen–halogen systems would be preferable in order to decrease the deposition temperature. Rudder *et al.*<sup>4</sup> and Kadono *et al.*<sup>5</sup> carried out radio-frequency (RF) and microwave plasma-assisted CVDs using mixtures of CF<sub>4</sub> and H<sub>2</sub>. Maeda *et al.*<sup>6</sup> also investigated the kinetics of the growth of diamond using mixtures of hydrocarbons, fluorocarbons and hydrogen. Frenklach *et al.*<sup>7</sup> found that chlorine was capable of abstracting residual hydrogen atoms from polycyclic aromatic compounds. Hong *et al.*<sup>2</sup> succeeded in synthesizing diamond at 380 °C by employing a hot-filament CVD method using CCl<sub>4</sub> and H<sub>2</sub>. Pan *et al.*<sup>8</sup> investigated the effect of chlorine on the formation of diamond by thermal CVD on a platinum substrate. The use of chlorine allowed the substrate temperature to be reduced by *ca.* 150 °C while maintaining the original growth rate without chlorine. Patterson *et al.*<sup>9</sup> reported that diamond was formed at 250–750 °C by thermally excited CVD in a tubular reactor using halocarbons. Tsang *et al.*<sup>10</sup> claimed that chlorine, which was added to a hot-filament CVD reactor, enhanced the abstraction of surface hydrogen rather than activating gas-phase reactions. Ando *et al.*<sup>11</sup> reported that fluorine abstracted hydrogen on the diamond surface at –10 °C and reacted with C=O bonds at temperatures > 100 °C. The diamond surface was fully fluorinated at 500 °C. They also reported that hydrogen atoms on the diamond surface were chlorinated at moderate temperatures.<sup>12</sup> Miller *et al.*<sup>13</sup> found that UV irradiation from an Hg lamp enhanced the chlorination of the hydrogenated diamond surface.

The above results suggest that halogens react with hydrogen atoms on the diamond surface at moderate temperatures, and that this technique has applications for the modification

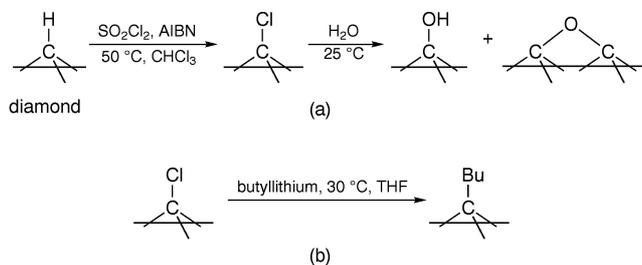
of diamond surfaces. Harrison *et al.*<sup>14</sup> calculated the friction of a diamond (111) surface onto which methyl, ethyl or *n*-propyl groups were introduced and predicted that the modified surface would be expected to show a lower friction coefficient than the hydrogen-terminated diamond (111) surface. Miyake *et al.*<sup>15</sup> reported that the friction of a polished polycrystalline diamond surface was reduced when the surface was fluorinated by RF plasma-assisted CVD.

As can be seen above, modifications of diamond surfaces are usually performed using dry processes. If diamond surfaces are modified by means of organic reactions at ambient temperature, however, the possibility of diamond-based molecular devices would be considerably increased.<sup>16</sup> In an earlier paper,<sup>17</sup> we reported the chlorination of carbons on the diamond surface by a radical reaction in dry chloroform and further modification of the surface with *n*-butyl groups. However, the effect of nucleophiles on substitution yields was not fully investigated. In the present study, diamond powder was chlorinated by organic reactions in the liquid phase. The resulting chlorinated diamond surfaces were then butylated with *n*-, *sec*- and *tert*-butyllithium at 30 °C. The surface coverage by butyl groups was evaluated by pyrolysing the modified diamond at various temperatures, followed by recovery of the pyrolysis products.

## 2 Experimental

Fine diamond particles, less than 0.5 μm in diameter, (Tomei Diamond Co., Japan) were washed in a heated acid mixture (H<sub>2</sub>SO<sub>4</sub>–HNO<sub>3</sub>) and were then used as the substrate. The surface area was determined to be 21.0 m<sup>2</sup> g<sup>–1</sup> by nitrogen adsorption at –196 °C using a BET unit (Shimadzu, Micromeritics ASAP 2000). The equivalent diameter was calculated to be 40.6 nm. Fig. 1(a) shows the reaction scheme for chlorination and oxidation of diamond. The diamond powder was first hydrogenated in hydrogen at 900 °C for 4 h. After hydrogenation, the powder (0.1 g) was suspended in a solution of 2,2'-azobisisobutyronitrile (AIBN, 50 mg), sulfur chloride (0.01 mol) and anhydrous chloroform (10 ml) at 50 °C in an atmosphere of argon. AIBN was added as a radical initiator and sulfur chloride served as the chlorinating agent. The chlorinated diamond was sensitive to moisture, even at room temperature, giving an oxidized diamond surface. In order to

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**Fig. 1** Reaction schemes on diamond surface: (a) chlorination; (b) alkylation

evaluate the degree of chlorination, therefore, the chlorinated diamond was intentionally oxidized, as indicated in Fig. 1(a), and C—OH and C—O—C absorbances of the oxidized diamond surface were determined by DRIFT spectroscopy (Perkin, Paragon 1000).

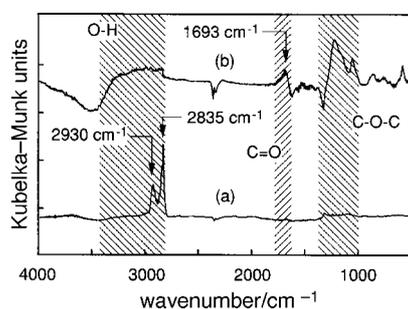
Fig. 1(b) shows the reaction scheme for the butylation reactions. After chlorination, the solution was exhaustively evaporated, and a solution of *n*-, *sec*- or *tert*-butyllithium in tetrahydrofuran (THF) was introduced into the flask containing the chlorinated diamond, without exposure to air. The butylation was carried out by stirring the suspension at  $30^\circ\text{C}$  for 4 h under an argon atmosphere. The reaction was then terminated by adding water to the solution. The powder was then repeatedly washed with THF and water to remove LiCl and other by-products, and the treated powder was then characterized by DRIFT spectroscopy.

Butyl groups incorporated on the diamond surface were decomposed using a Curie-point pyrolyser (Japan Analytical Ind., JHP22). A 5–7 mg portion of each sample was wrapped with a pyrofoil possessing Curie temperatures of 255, 358, 590, 764 and  $1040^\circ\text{C}$ , and was inductively heated at a rate of *ca.*  $3000^\circ\text{C s}^{-1}$  in a stream of nitrogen. The pyrolysis was maintained for 5 s at each Curie temperature, and all gaseous products were recovered and determined using a gas chromatograph.

### 3 Results and Discussion

#### 3.1 Chlorination of hydrogenated diamond surface

Fig. 2(a) and (b) show DRIFT spectra of the diamond powders, which had been hydrogenated and then chlorinated at  $50^\circ\text{C}$  for 8 h and then further oxidized by exposure to water. The assignments of hydrogen chemisorbed on the diamond {100} and {111} surfaces have been investigated<sup>18,19</sup> as cited previously.<sup>17</sup> Spectrum (a), without chlorination, shows peaks at 2930 and  $2835\text{ cm}^{-1}$ , which are assigned to C—H groups on the diamond {100} and {111} surfaces, respectively. Spectrum (b), of the chlorinated and oxidized diamond, shows a peak at  $1350\text{--}1000\text{ cm}^{-1}$ , which is assigned to a C—O—C ether group, and a peak at  $1693\text{ cm}^{-1}$ , which is assigned to a C=O group. A broad peak at  $3400\text{--}2800\text{ cm}^{-1}$  is assigned to O—H groups formed by reaction with water.



**Fig. 2** DRIFT spectra of chlorinated and then oxidized diamond: (a) without chlorination, (b) chlorinated for 8 h

No C—Cl stretching at  $800\text{--}600\text{ cm}^{-1}$  was observed for the oxidized sample.

Ando *et al.*<sup>20</sup> measured the weight gain of a hydrogenated diamond powder after gas-phase chlorination at  $250^\circ\text{C}$  and concluded that the weight gain was equivalent to 52–60% of that calculated, assuming that all surface carbons were substituted with chlorine. They further evaluated the degree of oxidation of chlorinated diamond by exposing the sample to ambient atmospheric conditions for periods of 5–180 min. Since they observed no peaks for C—H and C—Cl and observed only peaks corresponding to C—O—C and C=O, they concluded that the chlorine which had been bonded to diamond was completely oxidized at room temperature. In the present study, no changes in the DRIFT spectrum were observed after the hydrogenated diamond was exposed to water vapour at  $500^\circ\text{C}$ . The C—H peaks in spectrum (a) completely disappeared after chlorination and oxidation. The C=O and C—O—C peaks, therefore, were formed by oxidation of C—Cl bonds. Thus, the fraction of the chlorinated surface carbon atoms may be considered to be as high as that reported by Ando *et al.*<sup>20</sup>

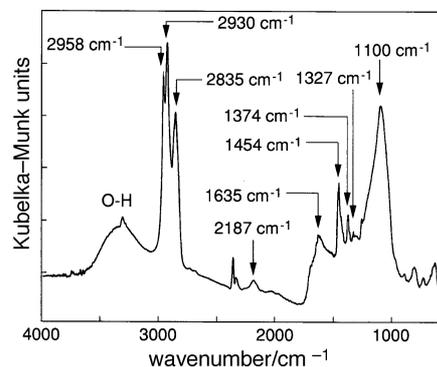
#### 3.2 Butylation of chlorinated diamond surface

Fig. 3 shows a DRIFT spectrum of the chlorinated diamond powder after treatment with *n*-butyllithium for 4 h. Peaks corresponding to C—H stretching at  $2958\text{ cm}^{-1}$  and C—H deformation at 1454, 1378 and  $1327\text{ cm}^{-1}$  were increased as a result of alkylation, suggesting that chlorine was replaced by an *n*-butyl group. Weak peaks at *ca.* 2200 and  $1700\text{--}1600\text{ cm}^{-1}$  were presumed to be assigned to alkyne and alkene, respectively, but this formation mechanism was not elucidated. An intense peak at  $1350\text{--}1000\text{ cm}^{-1}$  and a broad peak in the range  $3600\text{--}2800\text{ cm}^{-1}$ , assigned to C—O—C and O—H groups, respectively, appeared as a result of reaction between the remaining chlorine and water, when the sample was exposed to water.

Fig. 4 shows a DRIFT spectrum of the diamond powder treated with *sec*-butyllithium for 4 h. Again, peaks corresponding to C—H deformation at 1411 and  $1358\text{ cm}^{-1}$  increased, suggesting the introduction of *sec*-butyl groups. Peaks assigned to C—O—C and O—H groups also appeared. Fig. 5 shows a DRIFT spectrum for the case of *tert*-butyllithium. Peaks corresponding to C—H stretching appeared, and weak peaks corresponding to C—H deformation appeared. This suggests that *tert*-butyl groups, which contain three methyl groups and no methylene group, were introduced.

#### 3.3 Product distribution in the flash pyrolysis of butylated diamond surfaces

Fig. 6 shows the effect of pyrolysis temperature on product distributions for the *n*-butylated diamond. The major organic products were methane, ethylene, ethane, propylene, propane,



**Fig. 3** DRIFT spectrum of a chlorinated diamond powder treated with *n*-butyllithium for 4 h

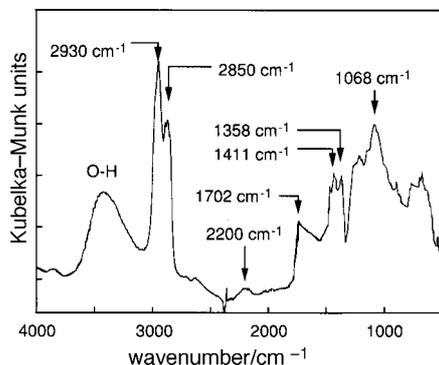


Fig. 4 DRIFT spectrum of a chlorinated diamond powder treated with *sec*-butyllithium for 4 h

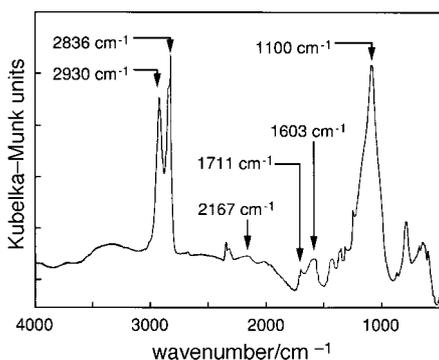


Fig. 5 DRIFT spectrum of a chlorinated diamond powder treated with *tert*-butyllithium for 4 h

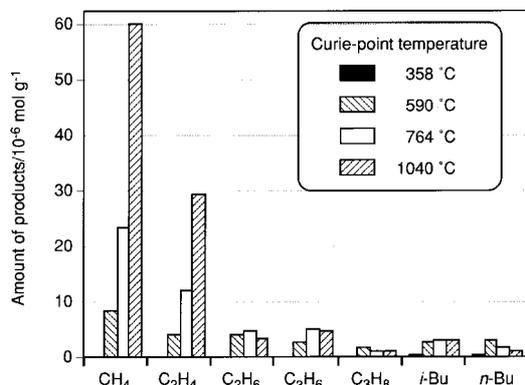


Fig. 6 Product distributions from *n*-butylated diamond powder by pyrolysis at 358, 590, 764 and 1040 °C

isobutane and *n*-butane. No organic products were detected at a pyrolysis temperature of 255 °C, suggesting that butyl groups on the diamond surface were chemically incorporated and not physically adsorbed. No methane was produced from the hydrogenated samples which had not been subjected to butylation, at all temperatures studied. Thus, the methane was produced by the fragmentation of incorporated butyl groups and not by cleavage of C—C bonds of the outermost surface of the diamond. The number of carbons produced by the pyrolysis per unit mass of diamond were  $3 \times 10^{-6}$ ,  $6.0 \times 10^{-5}$ ,  $9.3 \times 10^{-5}$  and  $1.30 \times 10^{-4}$  mol g<sup>-1</sup> at temperatures of 358, 590, 764 and 1040 °C, respectively. The number of butyl groups was then calculated by dividing the number of recovered carbon atoms by four. Matsumoto *et al.*<sup>21</sup> attempted to incorporate hydrogen, methane and ethane onto the diamond surface by exposing the diamond surface in an atmosphere of each compound at 1000 °C. They detected hydrogen and ethane using temperature-programmed desorption (TPD) after the treatment. However, the quantities of incorporated species were not determined. Fig. 7(a) and (b) show the schematic structure of the diamond {100} and {111}

surfaces, respectively.<sup>22</sup> The number of hydrogenated surface carbon atoms depends on the surface structure. If the diamond powder, having a total surface area of 21.0 m<sup>2</sup> g<sup>-1</sup>, possesses only the {100} or {111} surface, the number of hydrogenated surface carbons is 5.5 or  $6.4 \times 10^{-4}$  mol g<sup>-1</sup>, respectively. If the {100} and {111} faces appear equally, the number of hydrogenated surface carbon atoms is  $5.95 \times 10^{-4}$  mol g<sup>-1</sup>. The number of butyl groups recovered by the flash pyrolysis are converted to fractions of *n*-butylated surface carbons by dividing by the number of hydrogenated surface carbons. As shown in Fig. 8, the calculated values show an asymptote of 0.055, which is approximated by the value at a pyrolysis temperature of 1040 °C.

Fig. 9 shows the effect of pyrolysis temperature on product distributions by the Curie-point pyrolysis when *sec*-butyllithium is used as the butylating reagent. The number of carbons produced by pyrolysis was  $1.7 \times 10^{-5}$ ,  $5.2 \times 10^{-5}$ ,  $8.4 \times 10^{-5}$  and  $9.4 \times 10^{-5}$  mol g<sup>-1</sup> at temperatures of 358, 590, 764 and 1040 °C, respectively. Fig. 10 shows the product distributions for the *tert*-butylated diamond. When *tert*-butyllithium was used, isobutane was produced selectively. The number of carbons recovered were  $4 \times 10^{-6}$ ,  $5.6 \times 10^{-5}$ ,  $1.07 \times 10^{-4}$  and  $1.11 \times 10^{-4}$  mol g<sup>-1</sup> at pyrolysis temperatures of 358, 590, 764 and 1040 °C, respectively. The fractions of *sec*- and *tert*-butylated carbons, calculated based on the hydrogenated surface carbons, are also shown in Fig. 8. Thus, the fractions of surface carbons bonded with butyl groups, calculated from the total carbons recovered by pyrolysis at 1040 °C, were 0.040 and 0.047 for *sec*-butylation and *tert*-butylation, respectively.

The reactivities of the butanes used herein are controlled by steric effects and the stability of the intermediates. However, the present experiment indicates that the fractions of butyl-bonded surface carbons are nearly the same, irrespective of the structure of the butylation reagents. Thus, the rate-limiting step for the butylation may be elimination of chlorine from the surface carbon.

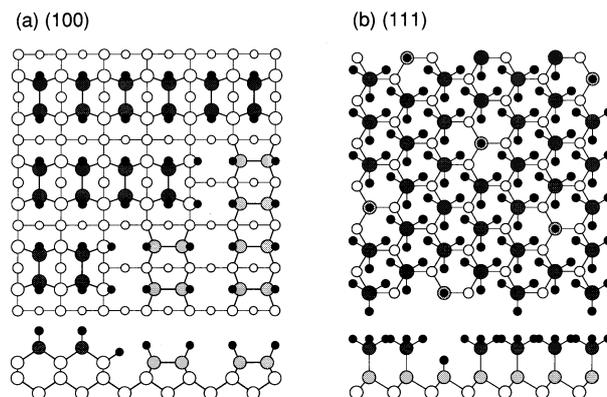


Fig. 7 Schematic structures of (a) {100} 2 × 1 diamond surface; (b) {111} diamond surface

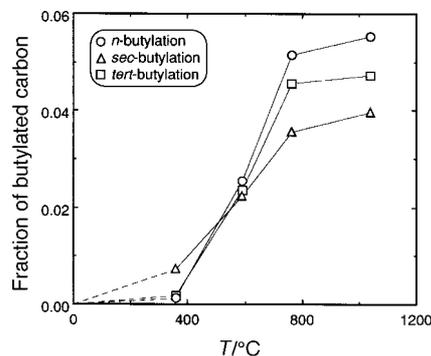


Fig. 8 Fractions of hydrogenated surface carbons substituted by *n*-, *sec*- and *tert*-butyl groups, calculated from products produced by pyrolysis at temperatures of 358, 590, 764 and 1040 °C

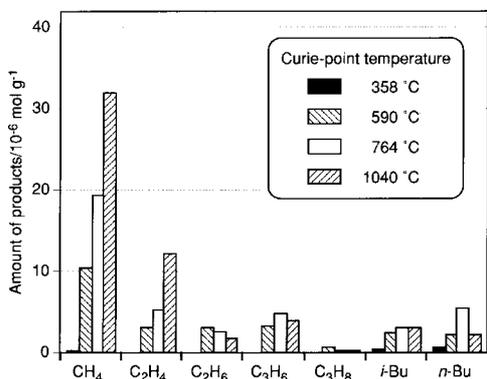


Fig. 9 Product distributions from *sec*-butylylated diamond powder by pyrolysis at 358, 590, 764 and 1040 °C

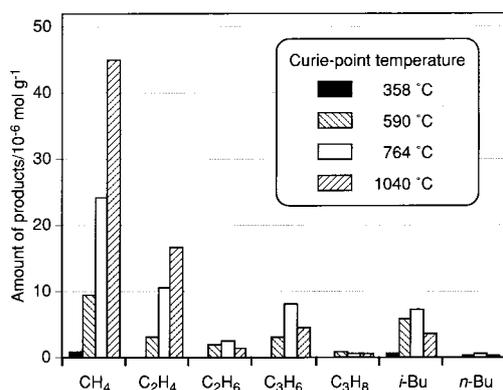


Fig. 10 Product distributions from *tert*-butylylated diamond powder by pyrolysis at 358, 590, 764 and 1040 °C

#### 4 Conclusions

Hydrogen atoms bonded to carbon atoms on the diamond surface were chlorinated by radical reactions in chloroform, and the chlorinated diamond was subsequently reacted with *n*-, *sec*- or *tert*-butyllithium in THF at 30 °C for 4 h in an inert atmosphere. The butyl groups which were incorporated onto the diamond surface were decomposed by flash pyrolysis at temperatures between 255 and 1040 °C. The fraction of butyl-

ated surface carbons to the total surface carbons was calculated to be 0.055 for *n*-butylation, 0.040 for *sec*-butylation and 0.047 for *tert*-butylation, based on flash pyrolysis experiments at 1040 °C. The fraction of surface carbons incorporated by functional groups may be increased by optimizing reaction conditions and by the careful selection of substituents.

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Paper 7/07905B; Received 3rd November, 1997