Control of crystallographic orientation in diamond synthesis through laser resonant vibrational excitation of precursor molecules

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Crystallographic orientations determine the optical, electrical, mechanical, and thermal properties of crystals. Control of crystallographic orientations has been studied by changing the growth parameters, including temperature, pressure, proportion of precursors, and surface conditions. However, molecular dynamic mechanisms underlying these controls remain largely unknown. Here we achieved control of crystallographic orientations in diamond growth through a joint experimental and theoretical study of laser resonant vibrational excitation of precursor molecules (ethylene). Resonant vibrational excitation of the ethylene molecules using a wavelength-tunable CO2 laser steers the chemical reactions and promotes proportion of intermediate oxide species, which results in preferential growth of {100}-oriented diamond films and diamond single crystals in open air. Quantum molecular dynamic simulations and calculations of chemisorption energies of radicals detected from our mass-spectroscopy experiment provide an in-depth understanding of molecular reaction mechanisms in the steering of chemical reactions and control of crystallographic orientations. This finding opens up a new avenue for controlled chemical vapor deposition of crystals through resonant vibrational excitations to steer surface chemistry.

Lasers are ideal energy sources for vibrational excitations because their narrow bandwidth prepares a single vibrational eigenstate, which makes precise control of reaction pathways feasible. One approach to laser control is active intervention, in which the phases of reagent motions are controlled during the course of the reaction. This active intervention may preferentially lead reagents to one of many different reaction routes. In this study, we introduced active intervention to material synthesis, and achieved control of chemical reaction and hence controlled crystallographic orientations through laser resonant vibrational excitations of precursor molecules in chemical vapor deposition (CVD) of diamond.

Due to its extreme properties, diamond has found widespread applications, including heat spreaders, optical windows, biosensors, and nano- or microelectromechanical systems (N/MEMS), as well as its promising potentials in quantum information technology. Many properties of diamond, including thermal conductivity, optical behavior, and mechanical properties, depend on diamond crystallographic orientations. Preferential growth of {100}-textured diamond films has been pursued for years because of their superior properties over those of the {111}- and {110}- textured diamonds. Mechanically, {100}-textured diamond films have lower roughness and higher wear resistance as compared with other crystallographic directions. Optical properties of {100}-textured films are superior to those of {111}-textured films in terms of refractive index and extinction coefficient. Research efforts have been exerted to achieve orientation-controlled growth of diamond. Liu et al. have studied control of diamond textures by varying the growth parameters, including substrate temperature, precursor...
concentration, and films thickness\(^4\). By applying bias-enhanced nucleation\(^{20,21}\) and introducing nitrogen into the growth precursors\(^{22-26}\), \(\{100\}\)-textured diamond films have also been successfully deposited. These methods are capable of producing \(\{100\}\)-textured diamond films with good reproducibility. However, the molecular reaction mechanism remains elusive and further investigations are needed to obtain in-depth understanding on the control of crystallographic orientation. In our previous study, resonant excitations of precursor molecules have been applied in the synthesis of diamond films and crystals\(^{27,28}\). Diamond growth rate and quality were obviously promoted. Diamond crystals with sizes up to 5 mm were successfully obtained in open air\(^{28}\). In-depth understanding of the laser control of chemical reactions and control of diamond crystallographic orientations are investigated in this research.

**Results and discussion**

We introduced resonant excitations of precursor molecules using a wavelength-tunable CO\(_2\) laser to steer the chemical reactions in diamond formation which in turn resulted in preferential growth of \(\{100\}\)-textured diamond of high phase purity. The diamond growth process was steered by resonantly exciting ethylene (C\(_2\)H\(_4\)) molecules to higher vibrational and rotational states. A schematic illustration of the experimental setup is shown in Figure 1a. The detailed experimental method is described in the Methods section. The wavelength of the tunable CO\(_2\) laser ranges from 9.2 to 10.9 µm. Figure 1b shows a representative absorption spectrum of the laser energy by the C\(_2\)H\(_4\)/C\(_2\)H\(_2\)/O\(_2\) flame with respect to the laser wavelength in the CO\(_2\) laser 00’-10’ emission band. Several absorption peaks were observed at different wavelengths. The strongest peak at 10.532 µm corresponds to the Q branch (\(\Delta J = 0\)) of a fundamental vibration mode (\(\nu_5\), CH\(_2\)-wagging) of the ethylene molecules\(^29,30\). Another absorption peak at 10.22 µm corresponds to the R branch (\(\Delta J = 1\)) of the CH\(_2\)-wagging mode\(^29,30\), which means that the molecules are excited to a higher level of vibrational state with a higher level of rotation energy, as schematically indicated in Figure 1c.

We compared the excitations of ethylene molecules in the combustion flame by laser irradiation at 10.22, 10.333 (non-resonant wavelength), and 10.532 µm, and deposited diamond films with all other parameters the same. Figure 2a–d show representative scanning electron microscopic (SEM) images of diamond films deposited for 15 (upper) and 60 min. (lower), respectively. Diamond films deposited without laser excitation were also included for comparison. Thicknesses of these diamond films are given in Figure S1 of the Supporting Information. It was observed that diamond films deposited by the 10.22 µm laser excitation exhibit predominantly \(\{100\}\) surfaces, while those deposited under the other three conditions showed random orientations. This phenomenon does not change with deposition time, as demonstrated by similar film morphology under each condition of different deposition time (15 and 60 min.). It is demonstrated that excitation of ethylene molecules through the
vibrational excitation of ethylene molecules at 10.22 μm leads to a preferential growth of [100]-textured diamond films. Under the resonant excitation at 10.22 μm, single crystal diamond with a size of 300 μm was grown in 5 hr. in open air, as shown in Figure 2e. Different from the diamond crystals deposited through vibrational excitation of ethylene at 10.532 μm28, this diamond crystal exhibits high uniformity. A flat [100] surface as shown in Figure 2f demonstrated the preferential growth of the [100] surface for long time deposition. No twinning was observable in the SEM images on the [100] surface. Twinning abundantly exist on the [111] surfaces (the four surfaces surrounding the [100] surface), which is believed to be caused by the faster growth in the [111] compared to that in the [100] direction15. The crystal shape of diamond facets is determined by the growth rate of the [100] direction (V_{100}) and that of the [111] direction (V_{111}), as indicated by the diamond growth parameter, V_{100} = \sqrt{3} V_{111}^{1.432}. The facets that show up at the final stage of crystal growth are those along which the growth velocity is the least. The growth velocity of the [111] direction should be greater than that of the [100] direction in order to obtain the predominantly [100] surfaces. It has been widely accepted in diamond growth that higher growth velocity in certain sector will result in lower phase purity in that sector, which results in the twinings on the [111] surfaces28,31,32. A lower concentration of twinings on the [100] surface indicates high quality of the [100]-oriented diamond crystals.

Raman spectroscopy was performed to determine the phase purity of the deposited diamond films and crystals. Figure 3a shows Raman spectra of the diamond films deposited for 60 min. under different excitation conditions. The shift of the diamond peak from 1332 (phase-pure natural diamond) to 1335 cm$^{-1}$ is ascribed to the residual stresses in the diamond films caused by differences in the coefficients of thermal expansion (CTE) between the diamond films and the substrates. The D-band is related to disordered carbon structures, and G-band corresponds to sp$^2$ graphite phases in the diamond films. It is obvious that both D- and G-bands are suppressed in diamond films deposited with laser excitations at 10.22 and 10.532 μm, indicating an increased purity of diamond sp$^2$ bonding. The spectrum of the diamond film deposited with laser excitations at 10.22 μm exhibits even lower D- and G-bands, indicating that the [100] surfaces have better phase purity than other surfaces. This is in agreement with the transmission electron microscopic (TEM) study of different diamond growth sectors, which revealed that the [100] sector has low density of dislocations, while the [111] sectors are highly defective, containing a high density of dislocations and stacking faults15. Figure 3b shows the Raman spectra of diamond crystals, including those deposited with 10.22 (shown in Figure 2e) and 10.532 μm excitations (reported in Ref. 25) as well as a type Ia natural diamond. The diamond peaks of these three crystals are all located at 1332 cm$^{-1}$. The D- and G-bands are invisible in all spectra, which indicate very high purity of the diamond sp$^2$ bonding. The full width at half maximum (FWHM) value of the [100]-oriented diamond is 3.3 cm$^{-1}$, which is similar to that of the natural diamond (3.1 cm$^{-1}$), much narrower than that of the diamond crystal deposited with the 10.532 μm excitation (4.5 cm$^{-1}$). Therefore, the [100]-oriented diamond crystal deposited with vibrational excitation of ethylene at 10.22 μm has high phase purity and high crystal quality.

Mass spectroscopy (MS) of the C$_2$H$_4$/C$_2$H$_2$/O$_2$ combustion flame used for diamond growth was performed under different excitation conditions to investigate mechanisms of the preferential growth of [100]-textured diamond, with more details described in the Methods section. Ionization of species occurs in the combustion flame, making the flame suitable for direct analysis using MS. Figure 4a shows a representative mass spectrum of the C$_2$H$_4$/C$_2$H$_2$/O$_2$ flame, in which positive ions with m/z values ranging from 12 to 47 are detected and assigned as CH$_x$$^+$ (x = 0~3), C$_2$H$_x$$^+$ (x = 0~5), C$_2$H$_x$$^-$ (x = 0~5), CH$_x$O$^-$ (x = 1~3) and C$_2$H$_x$O$^+$ (x = 2~5) ions. Considering differences in ionization potentials among different species, the height of each line does not necessarily represent the absolute concentration of each species. Nevertheless, MS analysis of the flame is valuable to determine the evolvement of species concentration under different excitation conditions, given that the variation of ions is proportional to that of related species. Figure 4b shows a chromatogram of the total ion current (TIC) of the C$_2$H$_4$/C$_2$H$_2$/O$_2$ flame under different excitation conditions, which provides the intensity of all detected ions in the flame. The TIC of the flame is a summation of all detected ions in the flame. By using the analysis tools as described.
for the trends, although relatively large deviation exists. The mean value for each wavelength is hence believed to be representative.

To gain molecular insights into relative abundances of produced species on different diamond surface, we computed the chemisorption energies of all species detected in the mass spectrometry experiment (CHx (x = 0 ~ 3), C2Hx (x = 0 ~ 5), CH2O (x = 1 ~ 3), and C2HxO (x = 2 ~ 5)) on the diamond C{100} and C{111} surface, respectively. Periodic density-functional theory (DFT) methods are employed (see Methods section). The chemisorption energies are shown in Table 1. Note that the chemisorption capacity can be used as an indicator of surface reactivity.24-26 Stronger chemisorptions lead to higher surface reaction activity. As shown from Table 1, the chemisorption of all species (except C2HxO with the least population, which is due to the perfect bond-length match with the C[100]-2×1 reconstruction surface) on the C{111} surface is much stronger than on the C{100} surface, indicating higher reactivity on C{111} surface and hence higher growth in the ⟨111⟩ direction than that in the ⟨100⟩ direction.

Figure 3 | Raman spectra of the diamond samples. (a), Diamond films deposited for 60 min without laser, with CO2 laser excitation at 10.22, 10.333 and 10.532 μm. (b), Diamond crystals grown for 5 hr with CO2 laser excitation at 10.22 and 10.532 μm. Natural diamond (type Ia) is also characterized as comparison. Inset, respectively show the FWHM of the diamond peak for each crystal.
the (100) direction. This favorable adsorption of hydrocarbon species on C\{111\}-1 \times 1 surface over the C\{100\}-2 \times 1 reconstruction surface is very similar to H- and OH- adsorptions on the relevant diamond surfaces\(^{36-38}\). Keep in mind that faster growth of one axial direction of crystals will result in larger areas of adjacent facets\(^{14,32}\). In this case, the growth rate in the (111) direction is higher than that in the (100) direction, resulting in larger area of the adjacent C\{100\} facets, which explains the predominant appearance of the diamond (100) surfaces.

To summarize, we have demonstrated a laser-assisted combustion process to synthesize (100)-oriented diamond films and single crystals through resonant vibrational excitation of precursor molecules. The CO\(_2\) laser beam at 10.22 \(\mu\)m excites the ethylene molecules to a higher vibrational state with higher rotational energy in the combustion flame, which increases the relative concentrations of the CH\(_x\)O and C\(_2\)H\(_x\)O species. Theoretical simulations of the reaction pathway indicate that these species react more easily with diamond (111) surfaces than with (100) surfaces, leading to a fast growth in the (111) direction and resulting in (100)-oriented diamond. This finding opens up a new avenue for controlled chemical vapor deposition of crystals through resonant vibrational excitation of precursor molecules.

**Table 1 | Calculated chemisorption energies (eV) on Diamond\{100\} and \{111\} surface with PBE/DNP method**

| Molecule | Chemisorption energy (eV) |
|----------|--------------------------|
|          | On C\{100\} | On C\{111\} |
| CHO      | -2.58          | -3.28        |
| CH\(_2\)O| -2.64          | -3.27        |
| CH\(_3\)O| -2.83          | -3.53        |
| C\(_2\)H  | -4.43          | -5.53        |
| C\(_2\)H\(_2\)| -3.75      | -4.60        |
| C\(_2\)H\(_3\)| -3.84      | -5.78        |
| C\(_2\)H\(_4\)| -3.13      | -3.99        |
| C\(_2\)H\(_5\)| -4.69      | -6.49        |
| C\(_2\)H\(_6\)| -6.09      | -3.53        |
| C\(_3\)H  | -4.04          | -4.34        |
| C\(_3\)H\(_2\)| -4.06      | -4.93        |
| C\(_3\)H\(_3\)| -2.35      | -2.76        |
| C\(_3\)H\(_4\)| -3.62      | -4.34        |
| C\(_3\)H\(_5\)| -5.18      | -6.35        |

**Figure 4 | Mass spectrometry of the C\(_2\)H\(_4\)/C\(_2\)H\(_2\)/O\(_2\) flame.** (a), Mass spectrum of the flame irradiated with CO\(_2\) laser at 10.22 \(\mu\)m. (b), Total ion current of the flame under different excitation conditions. (c), (d), Relative concentrations of CH\(_x\) (x = 0 – 3), C\(_2\)H\(_x\) (x = 0 – 5) ions (c), and CH\(_x\)O (x = 1 – 3), C\(_2\)H\(_x\)O (x = 2 – 5) ions (d).
Methods

Diamond synthesis. A combustion torch with a 1.5 mm orifice tip was used to produce diamond film. The precursor gas consisted of a mixture of C 2 H 2 (99.999%), C 6 H 6 (99.6%), and O 2 (99.996%), which were mixed in the torch through three gas flow meters (87920V, Spec Air Gases & Technologies). The gas flow rates of C 2 H 2, C 6 H 6, and O 2 were 0.62, 0.62, and 1.20 standard liters per minute (slpm), respectively. The CO 2 laser beam used to irradiate the flame was parallel with the substrate surface. The CO 2 laser beam was turned on after a local length of 1 mm was used to modulate the laser beam from its original diameter of ~13 mm to ~2 mm which is similar to the diameter of the flame (Figure 1a). The laser power density at the flame was around 10 5 W/cm². A tungsten carbide (WC) substrate (BS-65, Basic Carbide Corp., containing 6% cobalt) with a dimension of 12.7 × 12.7 × 1.6 mm 3 was placed on a top 4 atomic layers are fully relaxed) and another slab containing 9 atomic layers (the top 4 atomic layers are fully relaxed) (Figure 1d) and another slab containing 9 atomic layers (the top 4 atomic layers are fully relaxed). The DFT calculations are based on the Perdew-Burke-Ernzerhof (PBE) functional as described below. The DNP basis sets are considered as superior as the Gaussian 6-311 +G basis sets are.

The CO 2 laser beam used to irradiate the flame was parallel with the substrate surface. The DNP basis sets are considered as superior as the Gaussian 6-311 +G basis sets are. The effect of nitrogen on competitive growth mechanisms of diamond thin films. Diam. Relat. Mater. 9, 236–240 (2000).

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**Author contributions**

The first four authors contribute equally to this research. Z.X., J.P. and T.G. carried out the deposition and characterization of diamond films. J.B. and Y.G. carried out the theoretical simulations. Z.X. performed the MS analysis of the reaction. Z.X. and Y.Z. wrote the manuscript. Y.L., X.Z. and L.J. planned and supervised the study. All authors discussed the results and commented on the manuscript.

**Additional information**

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