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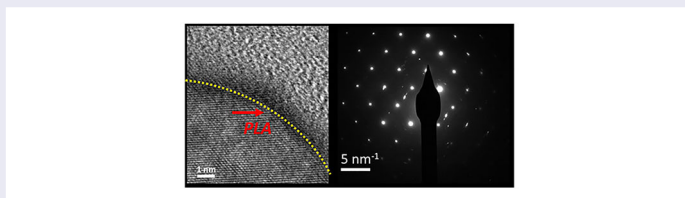
Direct conversion of Teflon into nanodiamond films

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ABSTRACT

We report a novel nonequilibrium approach for direct laser writing diamond by melting amorphous polytetrafluoroethylene (PTFE: $(C_2F_4)_n$) in ambient conditions. The nanosecond laser pulses disintegrate PTFE, forming the undercooled molten carbon. This undercooled molten carbon regrows into diamond during the ultrafast melt quenching process, which lasts for ~ 100 ns. HRTEM imaging, SAED, Raman, and EEL spectroscopy investigations confirm the first-order phase transformation of PTFE into single-crystalline $<110>$ oriented diamond, which is associated with ultrafast unseeded crystallization. Our experimental findings open up a new pathway for the selective conversion of organic polymers into nano and microdiamonds and thin films with laser-writing.



IMPACT STATEMENT

This research represents a fundamental breakthrough in selective conversion of PTFE polymeric films into single crystalline diamond thin films by pulsed laser annealing at near ambient conditions.

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KEYWORDS

Nanodiamond; laser annealing; transmission electron microscopy; Raman spectroscopy; molecular dynamics

Introduction

Diamond is an extraordinary material because of its exceptional mechanical, optical, and electronic properties. It exhibits record thermal conductivity (220 W/cm-K) with a wide-bandgap of 5.47 eV. Single-crystalline diamond is an ultimate semiconductor, considering its record Johnson (8200) and Keyes (32) figures of merit relevant for high-power and microelectronic devices, respectively, compared to 1 for Si. Particularly of interest are the NV and SiV nanodiamonds, which provide an ideal platform for quantum computing and nanosensing [1]. However, diamond is metastable at ambient conditions presenting formidable processing challenges in the fabrication of high-quality thin films. The idea of surface modification of these materials in ambient conditions and the consequent amorphous to crystalline transformation has driven decades of research. The phase transformation of graphite into diamond *via* equilibrium route requires very high temperature and pressure

(HPHT) conditions: 5000 K and 12 GPa, respectively [2]. These HPHT values can be lowered somewhat by using catalysts. The diamond thin film fabrication for solid-state devices relies on chemical vapor deposition (CVD), where diamond thin films are often contaminated with sp^2 bonded carbon.

The thermal transformation of organic compounds at high temperatures involves cracking reactions, molecular rearrangement, and degradation forming molten carbon with simultaneous loss of non-carbon species [3]. During graphitization, polymeric chains form graphite with defect states across C–C basal planes gradually getting annealed-off near 3300–3600 K. Interestingly, the application of pressure prevents sublimation, increasing the graphitic carbon yield. Notably, diamond conversion of polymeric materials like fluorene, polyethylene, and camphene has been shown by HPHT equilibrium-based approaches [4]. The thermal degradation of PTFE begins at 700 K and continues up to 1473 K [5]. It decomposes

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on heating at temperatures over 723 K with 0.9 GPa or higher pressures [6].

Laser annealing of polymers into diamond or graphene [7] with tunability in laser parameters provides an exciting dimension to materials processing, as these carbon polymorphs can be used in the development of novel devices. In the UV regime, photochemical absorption in PTFE results in molecular dissociation, while the longer wavelength light is absorbed in the vibrational modes. The fabrication of nanodiamonds by PTFE laser processing with higher pulse widths is plausible; however, the yield is small with less control and material degradation, due to the limited undercooling achieved and prolonged exposure to high temperatures [8]. These cost-effective methods have been employed to produce high quality graphene and nanodiamond composites for field emission applications [9,10]. The susceptibility towards sublimation [2] also presents a considerable bottleneck in carbon thermal processing. However, these thermodynamic bottlenecks can be overcome through kinetics considerations, by using ultrashort pulses to achieve melt processing near ambient conditions, due to the spatial and temporal confinement of the heat flow [11]. We have previously reported on the amorphous carbon phase transformation into diamond in ambient conditions [12] by utilizing liquid-phase regrowth of undercooled molten carbon. For undercooling > 1000 K, a new state of carbon: Q-carbon [13] is formed, which has a density of ~ 5.0 g/cc [14], and a mixture of randomized (75%–85%) sp^3 bonded carbon and remaining sp^2 . The pulsed laser annealing (PLA) approach results in molten carbon formation, which has been effectively employed to dope Boron upto 50 at.%, through solute trapping with diffusion coefficient of 10^{-4} cm²/s [15], which is much higher than the retrograde solubility limit of 2% [16]. In this case, PLA processing doped polymers can produce doped diamond thin films.

This study presents a novel route for PTFE conversion into diamond films by PLA processing at ambient conditions. The first-order phase transformation of PTFE into a single-crystalline diamond is a result of ultrafast regrowth of the undercooled carbon melt, at the laser annealing boundary. Thermodynamic considerations suggest that the low-energy phase transformation of graphite into diamond is challenging due to the positive value of the change in Gibbs free energy [17]. In PLA, the non-equilibrium approach of ultrafast quenching molten carbon results in the conversion of amorphous PTFE into diamond on increase in undercooling, which lowers the Gibbs free energy barrier. The PTFE and PLA processed diamond have been characterized by high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) imaging, selective-area

diffraction patterning (SAED), Raman, and local electron energy-loss (EEL) spectroscopy. Theoretical modeling of melting kinetics and microstructural evolution are performed by SLIM and *ab-initio* molecular dynamics. PTFE-based selective processing of diamond films by PLA will open a new frontier in coatings for electronic and photonic device applications.

Experimental

PTFE was laser annealed with Argon Fluoride Excimer laser ($\lambda = 193$ nm; pulse width = 20 ns) at 0.8 – 1.2 J cm⁻² energy density, and 1.0 ± 0.01 cm² spot size. After PLA, the PTFE was drop casted onto the ultrathin lacey carbon grid. Raman spectroscopy was performed with a Horiba-Jobin-Yvon LabRAM spectrometer, at 442 nm wavelength. The Raman spectra acquisitions were calibrated against the 520.6 cm⁻¹ Raman peak from (100) silicon. The structural modifications were analyzed by field-emission FEI Verios 460L SEM. HRTEM imaging and electron diffraction are performed using a FEI Talos-F200 microscope, with an 'XFEG' Schottky field emission gun source, operational at 200 keV. The electron energy-loss spectroscopy (EELS) scans were performed by using the EELS detector mounted in the STEM-FEI Titan 80–300 microscope, performed with an electron current of 35 pA collection angle of 25 mrad.

Results and discussion

Conversion of Teflon into diamonds

PLA processing at 1.0 J/cm² energy density transforms amorphous PTFE into diamond film and nanodiamonds. The structural transformation of PTFE on PLA processing is highlighted by employing a shadow mask to selectively convert PTFE into diamond, while the remaining PTFE film remains masked, as highlighted by the sharp boundary in Figure 1a-b. As the diamonds grow extremely fast, the tendency to undergo island growth generally results in nano and microrods. On tilt-correcting to 50°, the clear laser annealing boundary between the diamond rods and amorphous PTFE is revealed clearly in Figure 1b. The polymeric PTFE first unzips into monomers and dimers on initial laser irradiation, leading to a rise in absorbance with each subsequent pulse. Finally, the absorbance becomes high enough for the film temperature to reach ~ 4000 K and form undercooled molten carbon. The molten carbon quenches in < 100 ns during PLA processing, resulting in sharp phase boundaries and minimal interdiffusion. Usually, prolonged exposure of polymer coatings

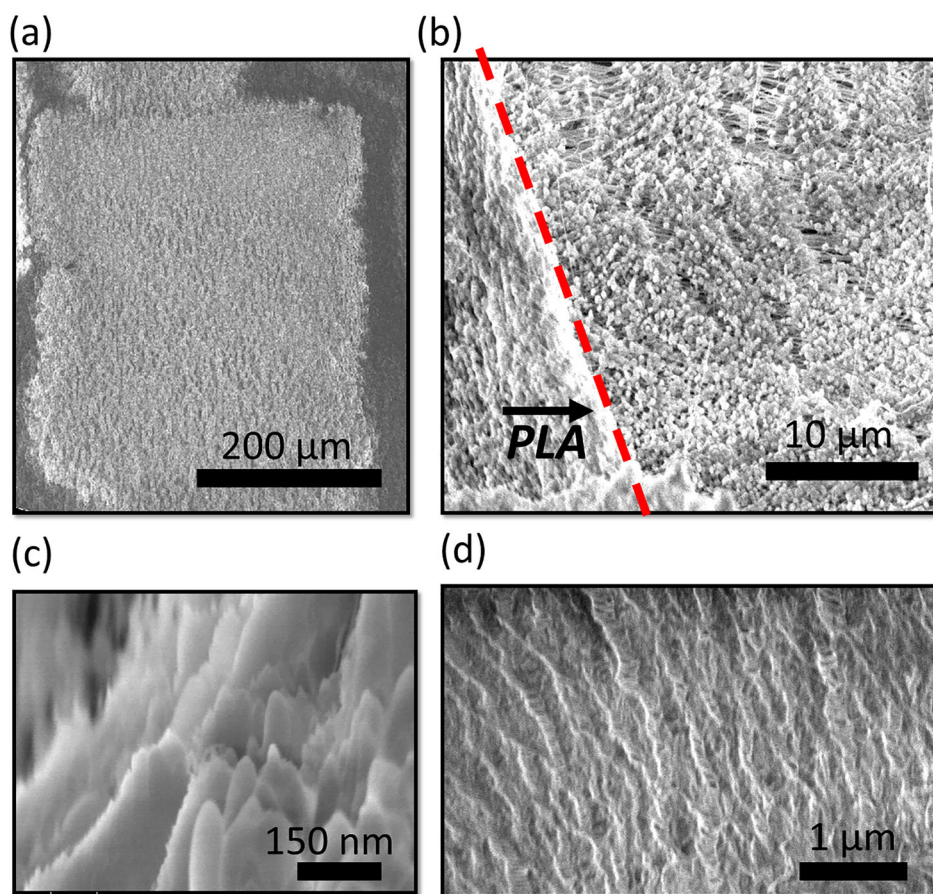


Figure 1. The FESEM images revealing (a) laser patterned boundary, on PLA processed PTFE film, (b) 50° tilt-corrected irradiated nanodiamond region and the PTFE boundary, (c) liquid phase regrown nanodiamonds and (d) as-acquired PTFE.

to high temperatures results in sublimation and material loss before it can be converted into diamond. As PLA processing entails heat flow in a single direction, and uniform melt front, the regrown diamond films are anticipated to be homogenous and single-crystalline, like the diamonds nucleating from the Q-carbon phase [18,19]. Figure 1c shows the 50° tilt-corrected HRSEM micrograph for the nanodiamonds. The rod-like characteristics of these diamonds suggest anisotropic growth along the $\langle 110 \rangle$ diamond chains [20]. Contrastingly, the uniform morphology of as-acquired PTFE suggests absence of diamonds, as shown in Figure 1d.

Raman spectroscopy

For diamond, the interpenetrating FCC lattices result in T_{2g} Raman vibrational modes at 1332 cm^{-1} . The C–C bond stretching in sp^2 hybridized carbon results in the emergence of vibrational G modes. The Raman spectrum for PLA processed films in Figure 2a reveals a major peak at 1326.9 cm^{-1} , which is the characteristic T_{2g} peak of the diamond phase [21]. The following equation is

used to calculate the nondiamond [22] contents in the diamond films:

$$C_{nd} = \frac{1}{1 + 75 \left(\frac{A_d}{A_{nd}} \right)} \quad (1)$$

Where, A_d represents the Raman peak intensity for diamond entities, and A_{nd} represents the Raman peak intensity for the non-diamond carbon content. The nondiamond content from peak deconvolution was found to be 0.36%. In diamond Raman spectrum, a red-shift is associated with phonon confinement, while a blue-shift arises due to strain considerations. Hence, the shift of 5.1 cm^{-1} is a result of phonon confinement along the z-axis in the diamond sheet [23]. In comparison, the microdiamond films formed by CVD processing Figure 2b, result in T_{2g} peak at 1332 cm^{-1} . The CVD processed microdiamond films exhibit a prominent G peak near 1550 cm^{-1} , which is non-existent in PLA processed diamond films. After PLA, there are additional peaks noted at 1170, 1363, 1432 and 1458 cm^{-1} . Figure 2c reveals the PTFE Raman spectrum with vibrational modes at 1215,

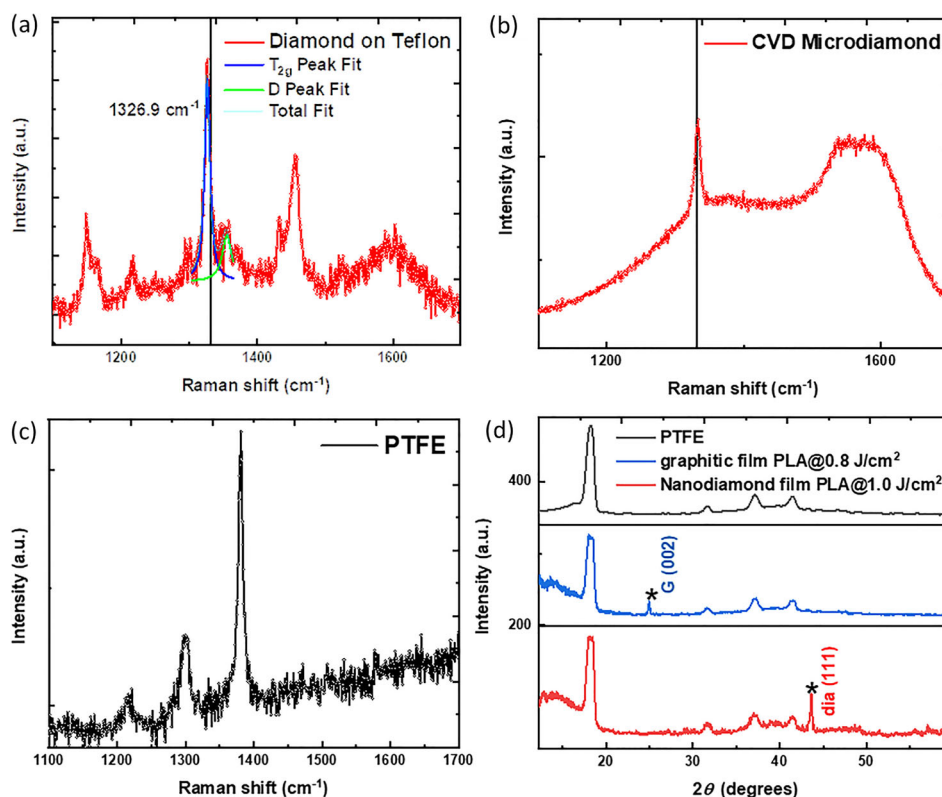


Figure 2. Raman spectroscopy of (a) nanodiamond sheet formed on PLA processing diamond, (b) CVD grown polycrystalline diamond and (c) PTFE, and (d) Reveals the XRD patterns for PTFE, PLA regrown diamond and graphitic films.

1300, and 1380 cm^{-1} . These vibrational modes arise due to the asymmetric E_2 (1215 cm^{-1}) and symmetric E_1 (1300 cm^{-1}) CF_2 stretching modes. Notably, the mode at 1380 cm^{-1} arises from depolarized A_1 symmetric CF_2 mode and has the most marked effect on the decrease in crystallinity [24]. The remaining peaks in PLA processed PTFE films match well with the $\text{CH}_3\text{-CH}_2\text{F}$ Raman spectrum, consisting of vibrational modes at 1170 cm^{-1} (A'), 1365 cm^{-1} (A'), and 1458 cm^{-1} ($A' + A''$) [25]. Correspondingly, XRD analysis is performed on PLA processed PTFE (Figure 2d), revealing formation of (111) out-of-plane oriented diamond.

Transmission electron microscopy

The conversion of amorphous PTFE into diamond is investigated by analyzing the atomic structure with plan-view HRTEM imaging (Figure 3a) and SAED pattern. The as-acquired HRTEM image of the diamond films at $\langle 110 \rangle$ zone-axis reveals an atomically-sharp interface between amorphous PTFE and crystalline diamond, which provides direct evidence of the first-order phase transformation of PTFE into diamond films. The low thermal conductivity of PTFE assists in achieving uniform undercooling in molten carbon for diamond regrowth. The out-of-plane $\langle 110 \rangle$ orientation of the

diamond sheet is related to rapid unseeded crystallization rather than seeded $\langle 111 \rangle$ growth through in-plane epitaxy on $\langle 0001 \rangle$ Al_2O_3 . The d_{111} spacing for diamond is ~ 2.06 Å, which agrees well with the HRTEM imaging analysis. The structural ordering in PTFE and laser annealed diamond is further investigated by fast Fourier transform (FFT) analysis (Figure 3a inset). It reveals the distinct primary (111 and 200) diffraction spots for the crystalline diamond, while PTFE exhibits diffused rings, arising from short-range ordering in the amorphous structure. The selected-area diffraction pattern (Figure 3b) acquired from the single-crystalline diamond region (in Figure 3a) presents no indication for the remanence of the amorphous carbon phase or PTFE. It reveals sharp diffraction spots, with the primary spots indexed as (1–11) and (11–1) family of planes, while kinematically forbidden (200) spots arise from double electron diffraction from (1–11) and (11–1) planes. The fact that SAED contains high-order Bragg reflections like (800) is indicative of good crystallinity. As expected, the high-resolution imaging of PTFE tape (Figure 3d) does not show any consistent lattice fringes due to its amorphous nature, which is also reflected in the associated SAED pattern in Figure 3c. The high-resolution imaging of diamond film in Figure 3d shows the lattice fringes arising from (111) family of planes with FFT

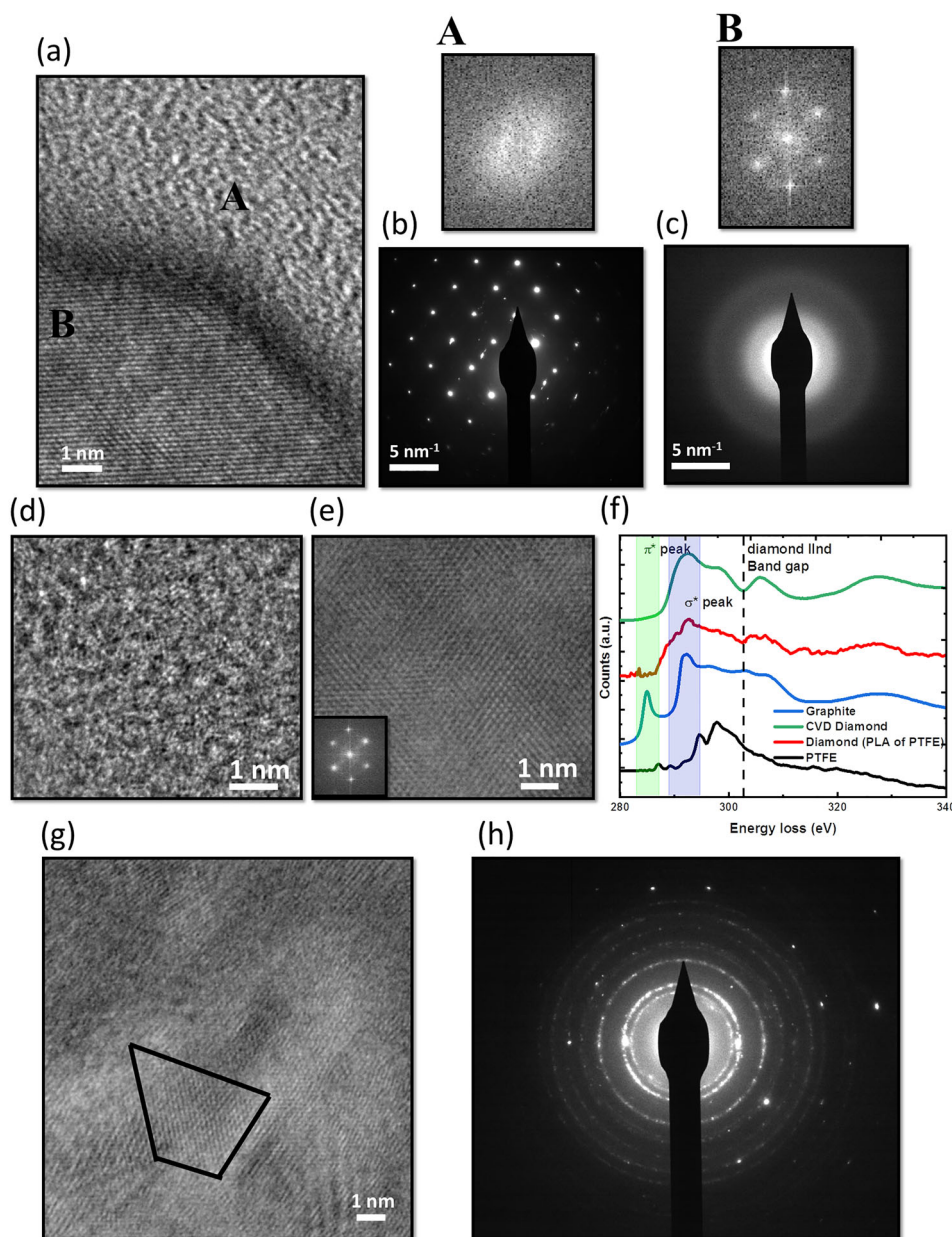


Figure 3. (a) Plan-view TEM image revealing atomically-sharp interface between $\langle 110 \rangle$ oriented diamond and amorphous PTFE. The inset in A and B show FFT pattern from PTFE and PLA processed diamond, respectively. (b) and (c) reveal the associated SAED pattern showing (111) and (200) spots for single-crystalline diamond nanosheet and amorphous PTFE with diffused rings, respectively. The corresponding HRTEM images show (d) amorphous PTFE and (e) single-crystalline diamond with (111) cross lattice fringes and associated FFT pattern in inset. (f) Reveals the acquired EEL spectrum from diamond nanosheet, bulk microdiamonds, amorphous Teflon tape and graphite. (g) and (h) reveal nanodiamond regrowth, and corresponding SAED pattern acquired from PLA processed PTFE at 0.8 J/cm^2 .

pattern (Figure 3e) is consistent with the SAED pattern in Figure 3b, containing the (111) and (200) spots.

Electron energy-loss spectroscopy

To further confirm diamond formation, high-resolution EELS scans are performed near the diamond/PTFE interface in Figure 3f. In EEL spectra of amorphous PTFE, C-K edge exhibits sharp peaks at ~ 287 and 289 eV

arising from the $1s \rightarrow \pi^*$ electronic excitation, while the peak at 292.2 is broadened due to the overlap of conduction bands. The peaks at 294.6 and 297 eV arise at much higher intensities due to the $1s \rightarrow \pi^*$ excitation arising from C-C and C-F bonds. The peak near 299.6 eV is related to the near-edge fine structure arising from the nearest neighbor C-C bonded atoms along the polymeric chain. The EEL spectra for carbon polymorphs constitute an initial peak arising from the π^*

antibonding states, and a second peak corresponds to σ^* antibonding states. The electronic transition from $1s$ to π^* and σ^* in carbon are reflected in first and second core-loss EEL spectral peaks, respectively. Figure 3f also shows a strong $1s-2p(\pi^*)$ transition ~ 284 eV in graphite, whereas the $1s-2p$ transition (σ^*) dominates the nanodiamond EEL signature ~ 297 eV [26]. In diamond EEL spectrum, the absence of π^* peak reflects its phase-pure crystalline nature. The sharp σ^* antibonding peak ~ 290 eV is a signature for diamond formation, observed in both CVD and PLA processed nanodiamonds. There is also a characteristic drop ~ 302 eV, arising from the absolute second bandgap in diamond.

Together with diamond films, nanodiamonds embedded in disordered graphene are formed at 0.8 J/cm^2 PLA energy density. The presence of disordered sp^2 bonded carbon with nanodiamonds suggests close-to-surface melting [27]. The HRTEM image for nanodiamond with cross-lattice fringes is shown in Figure 3g. For nanodiamonds, the SAED is speckled, with concentric rings arising from (111), (200), (220), (311), (222), (004), (331), and (333) planes (Figure 3h). As no diffused rings are observed in this SAED, it is evident that amorphization has not occurred, and the regrowth velocity is expected to be 4–6 m/s. During PLA, PTFE melts and forms the undercooled molten carbon. The undercooling shifts graphite/diamond/liquid carbon triple point from 5000 K/12 GPa to 4000 K/atmospheric pressure, also increasing the molten carbon Gibbs free energy, making it energetically favorable to form diamond.

Laser-solid interaction modeling

The laser-solid interactions are analyzed by SLIM programming [28,29] to understand the PTFE phase transformation into diamond. The thermal losses (radiative and conductive) were integrated into the PLA simulations with adiabatic boundary approximation. The parameters used for the SLIM simulation are carbon melting point (4000 K), molten carbon absorption coefficient ($8 \times 10^5/\text{cm}$), and laser pulse-width of 20 ns. Once melting occurs, the physical properties of molten carbon are utilized, as above 3000 K, PTFE completely disintegrates into carbon with F_2 evolution [6]. The thermal conductivity of molten carbon and amorphous PTFE are 290 and 0.25 W/mK , with reflectivity of 0.05 and 0.7, respectively. Interestingly, the low absorption coefficient of crystalline PTFE in the UV regime (250 cm^{-1} at 193 nm) results in non-melting, even for single pulse PLA at 1 J/cm^2 , as simulated in Figure 4a. However, we were able to irradiate and melt PTFE, as the white amorphous PTFE tape has the associated mid-gap states, which

increase absorption *via* the two-photon process. Successful ablation of PTFE and conversion into graphitic carbon was reported on multiple-pulse irradiation with 248 nm nanosecond lasers with absorption coefficient rising to $15,000 \text{ cm}^{-1}$ [30]. Notably, photon energy absorption and polymer degradation compensate for the low absorption coefficient. Notably, the findings resulted in an ablation threshold of 4.0 eV per monomer, hence on degradation and unzipping of the $-\text{CF}_2-$ chains, the absorption coefficient increases, and the process becomes single-photon-absorption driven. In our procedure, as we operated at $0.8\text{--}1.0 \text{ J/cm}^2$ laser fluence, an absorption coefficient of 7500 cm^{-1} was utilized.

The temperature-time profiles in Figure 4a suggests 0.8 J/cm^2 as the threshold energy density (E_d) to melt amorphous PTFE. This condition is ideal for regrowth of nanodiamonds with graphene-related materials. On the termination of laser pulse the melt front recedes. The ultrafast laser annealing process is ideal for processing materials like carbon, which sublimate on equilibrium-based processing under elevated temperatures, protecting it from reacting with oxygen in the densely-packed undercooled state. The rise in undercooling associated with molten carbon controls the regrowth of graphene, diamond [18], or Q-carbon. Post onset of melting, Figure 4b reflects a rise in melt depth with an increase in melt lifetime at 1.0 J/cm^2 PLA energy density. Notably, the liquid-phase regrowth of high-quality diamond sheets is controlled by the uniform undercooling associated with the carbon melt, which subsequently undergoes ultrafast quenching.

Ab-initio MD simulations

The liquid carbon was cooled rapidly under the canonical (NVT) ensemble, with a Langevin thermostat under isotropic pressure [31]. This liquid quench method is typically utilized to simulate metastable phases on ultrafast quenching liquids [32]. In ultrafast quenching processes, the undercooling of the melt is critical in controlling the final quenched structure [14]. As it is hard to manifest undercooling in molecular dynamics simulations, external isotropic pressure was used to densify the molten carbon. The modifications in molten carbon on quenching are analyzed using the radial distribution function (rDF) (Figure 5a), under isotropic pressure of 50 GPa by modulating the quench rates to study the tetrahedral diamond structural evolution with melt lifetime. Figure 5a reveals the generation of ordering as the melt lifetime increases from 25 ps, 250 ps, and 50 ns. The average sp^3 content is calculated from rDF profiles by using a radial at $1.85 \text{ \AA}$, resulting in $\sim 98\%$ sp^3 content, suggesting the formation of an amorphous diamond-like structure. In

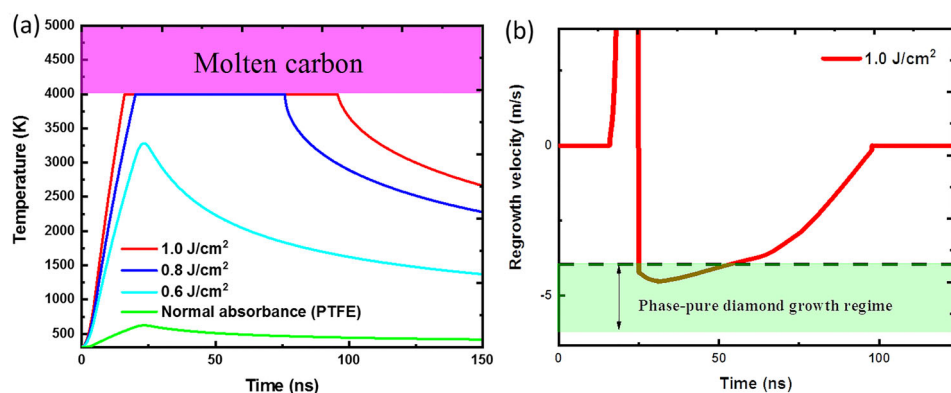


Figure 4. (a) The temperature vs. time plots for laser annealing PTFE tape at various energy densities; (b) melt depth vs. time for PLA energy density of 1.0 J/cm^2 .

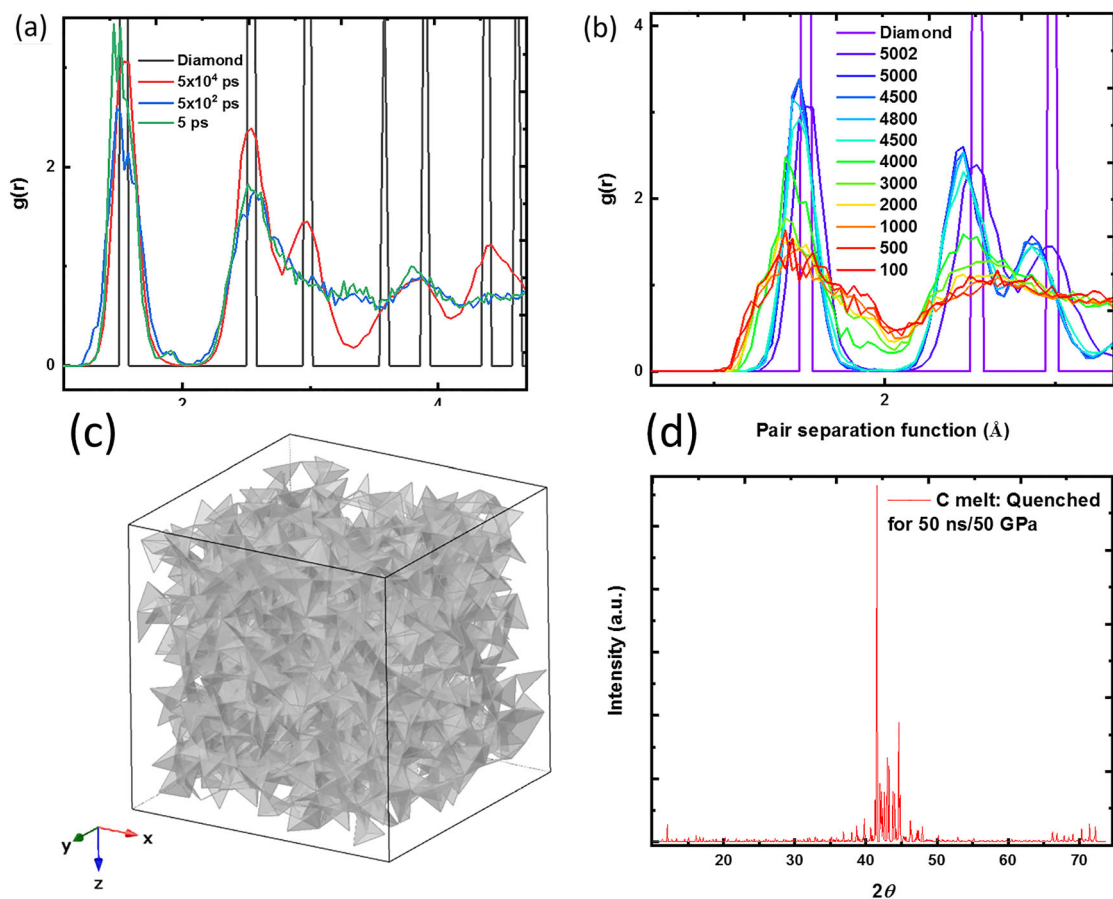


Figure 5. (a) highlights the modifications in rDF of molten carbon at 50 GPa, as a function of quenching rates; (b) shows rDF evolution during the pressurized quench, forming tetrahedral carbon; (c) shows the simulated structure with XRD pattern in (d).

the rDF profiles, once the formation of molten carbon occurs, a hump is noted, suggesting the evolution of disordered liquid carbon. Figure 5b reveals the evolution of molten carbon structure, as a function of simulation timesteps in subsequent rDF plots. With the progression of simulation timesteps, the structure of molten carbon stabilizes with a reduction in system entropy during the quenching cycle under pressure, resulting in conversion

into tetrahedrally-bonded carbon. Figure 5d shows that the simulated tetrahedrally bonded structure (Figure 5c), formed on quenching for 50 ns (10^{11} K/s quench rate), exhibits a major peak at $2\theta = 41.5^\circ$ (2θ for (111) reflections in diamond is $\sim 43.9^\circ$). These simulations reveal that molten carbon can be transformed into nano and microdiamonds on ultrafast quenching, by controlling the external conditions and melt quench lifetime.

Conclusions

Single-crystal nanodiamond films and nanocrystallites were fabricated by nanosecond laser annealing amorphous PTFE. The PLA processing of PTFE generates temperature > 4000 K for ultrashort timescales, forming undercooled molten carbon above 0.8 J/cm^2 . This molten carbon regrows into nanodiamond films due to the high undercooling achieved at the molten carbon/PTFE interface. The nanodiamonds exhibited a characteristic Raman peak near 1327 cm^{-1} , while the residual PTFE film disintegrated into fluoropolymers, following the established unzipping mechanism. The first-order phase transformation and the atomically sharp amorphous PTFE/single-crystalline diamond interface established the fact that the melting of PTFE indeed occurs on multiple-pulse PLA processing with increased degradation and absorption coefficient. This work provides a definite pathway for direct phase transformation of amorphous organic polymers into molten carbon, thereby forming diamond or graphene with modifications in undercooling.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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