Laser-induced phase separation of silicon carbide

Insung Choi1,2,*, Hu Young Jeong3,4,*, Hyeyoung Shin5, Gyeongwon Kang5, Myunghwan Byun1, Hyungjun Kim5, Adrian M. Chitu6, James S. Im6, Rodney S. Ruoff7,8, Sung-Yool Choi2 & Keon Jae Lee1,7

Understanding the phase separation mechanism of solid-state binary compounds induced by laser-material interaction is a challenge because of the complexity of the compound materials and short processing times. Here we present xenon chloride excimer laser-induced melt-mediated phase separation and surface reconstruction of single-crystal silicon carbide and study this process by high-resolution transmission electron microscopy and a time-resolved reflectance method. A single-pulse laser irradiation triggers melting of the silicon carbide surface, resulting in a phase separation into a disordered carbon layer with partially graphitic domains (~2.5 nm) and polycrystalline silicon (~5 nm). Additional pulse irradiations cause sublimation of only the separated silicon element and subsequent transformation of the disordered carbon layer into multilayer graphene. The results demonstrate viability of synthesizing ultra-thin nanomaterials by the decomposition of a binary system.

1Department of Materials Science and Engineering, KAIST, Daejeon 34141, Republic of Korea. 2School of Electrical Engineering, Graphene/2D Materials Research Center, Center for Advanced Materials Discovery for 3D Display, KAIST, Daejeon 34141, Republic of Korea. 3UNIST Central Research Facilities (UCRF), UNIST, Ulsan 44919, Republic of Korea. 4School of Materials Science and Engineering, UNIST, Ulsan 44919, Republic of Korea. 5Graduate School of Energy, Environment, Water, and Sustainability (E2WS), KAIST, Daejeon 34141, Republic of Korea. 6Program in Materials Science and Engineering, Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA. 7Center for Multidimensional Carbon Materials, Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea. 8Department of Chemistry, UNIST, Ulsan 44919, Republic of Korea. * These authors contributed equally to this work. Correspondence and requests for materials should be addressed to S.-Y.C. (email: sungyool.choi@kaist.ac.kr) or to K.J.L. (email: keonlee@kaist.ac.kr).
Laser beam-induced processing of materials has been utilized for tuning material properties due to the ability to rapidly heat to the melting point and it allows the controlled surface modification of materials. Laser thermal processing has been used to activate dopants introduced by ion implantation to modify the intrinsic properties of semiconductor materials such as Si and Ge to form ultra-shallow junctions. Further, laser beam-induced melting and solidification aids the fabrication of low-temperature polycrystalline silicon on glass or flexible substrates, which is well-established in producing thin film transistors for displays. Though many fundamental research studies related to an understanding of laser-induced phase transformations in elements have been made, laser interactions with binary compounds have been less studied because of the relative complexity of the compound materials.

The thermal decomposition of silicon carbide (SiC) has demonstrated a possibility for the direct synthesis of high-quality graphene on an insulating substrate. However, the extremely high temperature (~2,000 K) needed for conventional furnace processing limits its compatibility with industrial semiconductor applications. In this respect, excimer laser irradiation can be an alternative technique for the thermally driven surface reconstruction of SiC. Recently, several research groups have reported a sublimation of Si atoms on a SiC surface under nanosecond pulsed laser irradiation for the synthesis of graphene. However, an understanding of the graphitization mechanism has not been achieved due to the difficulty of observing the time sequence of the laser-induced decomposition of the binary compound into each elemental material.

Here we demonstrate the melt-mediated phase separation and surface reconstruction of single-crystal 4H-SiC by irradiation of a xenon chloride (XeCl) excimer laser (λ = 308 nm, pulse duration ~30 ns), resulting in formation of ultra-thin elemental material. Time-resolved reflectance (TRR) analysis shows an explicit information on the melting and solidification of 4H-SiC surface by laser irradiation. A single-pulse irradiation of laser fluence (that is, laser energy per unit area, 1.653 mJ cm^-2) allows the 4H-SiC surface to be melted and leads to the phase separation of liquid SiC into a disordered carbon (C) layer with graphitic domains (~2.5 nm) on a polycrystalline silicon (poly-Si, ~5 nm) layer in nanoseconds. Through molecular dynamics (MD) simulations, we confirm that graphitic C had the lowest surface potential energy in Si-C binary systems. Irradiation with a second pulse causes sublimation of only the separated Si, while the disordered C layer is transformed into a layered structure with increased crystallinity. These results are systematically investigated by high-resolution transmission electron microscopy (HRTEM), demonstrating that additional pulse irradiations lead to a gradual increase in the thickness of C layer, eventually to form multilayer graphene. Our study indicates the potential for nanomaterial synthesis through the phase separation of a binary compound by laser-induced melting and solidification.

**Results**

**Cross-sectional TEM analysis of phase separation.** To examine the phase separation and surface reconstruction of single-crystal 4H-SiC with laser irradiation, cross-sectional TEM observations were made. A platinum (Pt) thin layer was deposited to protect the top surface before sample preparation using focused ion beam milling. Figure 1a is a bright-field TEM image of a 4H-SiC surface irradiated by a single pulse from the laser, showing distinguishable layers formed on the original substrate (see details in Methods). To clearly identify these regions, we acquired HRTEM images using a spherical aberration-corrected TEM operated at 80 kV. A HRTEM image (Fig. 1b) shows that the brighter region of Fig. 1a is composed of two different phases (that is, C (~2.5 nm) and Si layers (~5 nm)); the former is referred as a randomly stacked, layered C structure and the latter is poly-Si with clear lattice fringes over a local area. A fast Fourier transform pattern shows that there is a 3C-SiC layer with the A–B–C stacking sequence between the poly-Si layer and the 4H-SiC surface. (Supplementary Fig. 1). In Fig. 1c, the poly-Si phase is confirmed by a high-magnification HRTEM image and fast Fourier transform patterns with (111) and (220) reflections. The top surface layer is observed to be disordered C with partially graphitic domains. To identify the C and Si layers, we used an energy-filtered TEM (EFTEM) for elemental mapping analysis (Fig. 1d). C mapping shows that the top layer on the surface consists of only C element without Si detection. In contrast, Si mapping shows the formation of a Si layer between the C and the SiC substrate, thereby demonstrating phase separation into C and Si layers. The atomic volume ratio of graphitic C to cubic Si was calculated to be ~1.2 (see Methods) corresponding to the thickness ratio of C (~2.5 nm) and Si layers (~5 nm), as shown in Fig. 1b. In addition, a HRTEM image (Fig. 1e) of the interfacial region between 3C and 4H-SiC shows that (111)-oriented 3C-SiC was epitaxially grown on (0001)-oriented 4H-SiC.

**MD simulations for phase separation process.** In an attempt to theoretically understand the origin of the melt-mediated phase separation of SiC, MD simulations were performed. To capture the key intermediates during the melting and solidification, which can be hardly sampled from a brute-force MD simulation, we manually built structures corresponding to the initial, intermediate and final states over the course of phase separation (full details about the structures are given in the Methods section). Each state of them was equilibrated by performing a MD simulation, and then minimized to obtain the energy. We considered eight different intermediate states connecting from the initial solid state of SiC (SiC (s), Supplementary Fig. 2) to the final state, where most C atoms are graphitized from the liquid phase of SiC (SiC (l)).

We found that the SiC (s) has the most stable energy, while the intermediate state where no carbon is yet graphitized from SiC (l) has the most unstable energy. Although the energy becomes gradually lowered as the graphitization process proceeds, multilayer graphene of the final state is still unstable compared with the SiC (s), as schematically shown in Fig. 2 (for details see Supplementary Fig. 3). This illustrates the energetic changes accompanied with the phase separation process; laser irradiation on the SiC (s) leads to the formation of highly unstable SiC (l) due to the heating up to ~3,500 K (Supplementary Fig. 4). This triggers the system to reach a metastable state with the formation of multilayer graphene. In addition, we found that graphitic C layer has the lowest surface energy in the Si-C binary system from an analysis of the atomic potential energy spectra of the systems (Supplementary Fig. 5), which can be understood as the driving force for the graphitization process. From these theoretical investigations, we conceive that the highly non-equilibrium character of the laser thermal processing helps the process be kinetically controlled, inducing a phase transform to the metastable state.

**TRR analysis for melt-mediated phase transformation.** The TRR analysis was used to identify the melt-mediated transformation by using the different reflectivities of the solid and liquid phases (see details in Methods and Supplementary Fig. 6). The inset in Fig. 3 shows an optical microscope image of the laser beam-irradiated area, 1 × 1 mm^2, which was used to measure the TRR signal. The TRR signal (Fig. 3) is increased from 50 to 75 ns by supplying the second hump (peak) of the laser pulse, indicating melting of 4H-SiC surface. The unusually high...
Intensity at 75 ns is estimated to include a reflectance signal from the 4H-SiC surface and laser signal (see Supplementary Note 1 for details). A plateau region between 180 and 450 ns indicates the presence of a liquid Si layer on the surface. This plateau region strongly suggests that the phase separation occurred within 180 ns (see Supplementary Note 1 for details).

Effect of an additional irradiation pulse. We examined a 4H-SiC surface irradiated with an additional pulse (the second, 1 Hz of laser pulse frequency) to obtain additional phase separation and reconstruction through a melt-mediated phase transformation. A bright-field TEM image (Fig. 4a) shows a thin layer with bright contrast and the formation of a 3C-SiC layer on 4H-SiC. Compared with single-pulse irradiation, a HRTEM image (Fig. 4b) of the top surface in Fig. 4a indicates the absence of a poly-Si layer and a graphitic C layer with increased crystallinity. Electron energy loss spectroscopy (EELS) analyses were performed to compare the crystallinity of the two samples (Fig. 4c). The C layer formed by the second irradiation pulse had increased crystallinity with a sharper $\sigma^*$ peak compared with that produced by single-pulse irradiation. The local non-uniform area on the 4H-SiC surface (Supplementary Fig. 7a) was investigated with a HRTEM to explain how the poly-Si layer observed in Fig. 1b disappears. A high-magnification image (Supplementary Fig. 7b) of an island structure, stacked on the 3C-SiC surface, indicates a residual poly-Si layer covered by an extremely disordered C layer. Additional analyses with EFTEM elemental mapping using C K- and Si L-edges clearly shows some remaining Si (Supplementary Fig. 7c,d). From these observations, we propose that Si atoms under a strongly bonded C layer rarely escape through the C layer because of the extremely short annealing time. Therefore, the disappearance of elemental Si below the C layer can be attributed to the sublimation of the...
poly-Si layer (melting point, \( m_p \approx 1,700 \text{ K} \)) induced by the laser fluence of \( \sim 1,653 \text{ mJ cm}^{-2} \), which is high enough to melt the SiC (\( m_p \approx 3,100 \text{ K} \)). In contrast, C material is remained on the surface due to its extremely high melting temperature (\( m_p \approx 4,000 \text{ K} \)).

Figure 4d shows the TRR signal of a surface that was irradiated with the additional pulse (the second) on the disordered C/poly-Si/3C-SiC/4H-SiC structure shown in Fig. 1b. The TRR signal is noticeably increased at 37 ns as soon as the first hump of the second laser pulse was incident on the surface. We assume that the high intensity at 37 ns is due to a sublimation of the separated poly-Si layer. The flattened region between 150 and 290 ns clearly indicates liquid SiC (see Supplementary Note 2 for details). The inset in Fig. 4d compares the TRR signals of single and the second irradiation pulses. Note that the higher intensity and longer flattened region of the TRR signal, observed only in the single-pulse irradiation, are related to the generation of separated Si element.

Investigation of multi-pulse irradiations. To investigate the formation process of multilayer graphene, multi-pulse irradiations were carried out and characterized. Figure 5a,b shows HRTEM images of 4H-SiC surfaces after 3 and 10 irradiation pulses, respectively. Both clearly show no further phase separation and new surface reconstruction, compared with single or two irradiation pulses. From these observations, we believe that additional phase separation cannot be developed by multi-pulse irradiations because the C layer, which has the lowest surface energy, has already been formed by the first irradiation pulse. On the other hand, the 4H-SiC surface with 10 irradiation pulses (Fig. 5b) shows an increased thickness of the C layer, which corresponds to multilayer graphene, while the thickness of the 3C-SiC layer decreases. To verify the thickness changes in the C and 3C-SiC layers with the number of irradiation pulses, TEM analyses were performed for the samples irradiated with 1, 2, 3, 10, 30 and 100 pulses. Figure 5c shows the thicknesses of the C (blue line) and 3C-SiC layers (black line) as a function of the number of pulses. The thickness of the C layer (\( \sim 2.2 \text{ nm} \)) formed by single-pulse irradiation was slightly decreased (\( \sim 1.3 \text{ nm} \)) after the second irradiation pulse due to an improvement of the crystallinity with \( sp^2 \) bonding. The average thickness (square label) of the C layer increased gradually after the tenth pulse, while the 3C-SiC layer became thinner.
HRTEM images and Raman data for laser irradiation up to 300 pulses are shown in Supplementary Fig. 8. Three representative peaks at Raman spectra, including the defect-induced D peak, in-plain vibrational G peak and two-phonon scattered 2D peak are clearly observed at 1,364, 1,583 and 2,720 cm⁻¹, respectively. By increasing the number of irradiation pulses, intensity of two-phonon scattered 2D peak is increased while D peak is decreased. EELS analyses were used to characterize the improvement in the crystallinity of the C layer (Supplementary Fig. 9). The EELS spectrum for 100 pulses is comparable to that of chemical vapour deposition-grown multilayer graphene with a random stacking. In addition, the TRR signals for 4H-SiC surface with many irradiation pulses (Fig. 5d) were examined to characterize the melting and solidification process. All TRR data show a flat region that indicates melt-mediated decomposition and solidification of the 4H-SiC surface for the formation of multilayer graphene (see Supplementary Note 3 for details).

Discussion
We have investigated XeCl excimer laser–SiC interaction to understand decomposition mechanism of solid-state binary compound by using a wide range of laser fluences and various number of irradiation pulses. Supplementary Fig. 10 shows HRTEM images of 4H-SiC surfaces after single and multi-irradiation of laser fluence E1, E2 and E3 corresponding to 1,000, 1,200 and 1,653 mJ cm⁻², respectively. We found two major regimes of amorphization and phase separation by single-pulse irradiation, which strongly depend on laser fluence. Low laser fluences of E1 and E2 induced formation of thin amorphous layers, such as ~3 and ~17 nm (Supplementary Fig. 10a,b), through melting and quenching process. To investigate the relationship between the number of laser pulses and formation of graphitic C layer, multi-irradiation pulses with E1 and E2 were performed. Although many pulses up to 600 were irradiated on 4H-SiC surface, no graphitized C layer was observed at the laser fluence E1 (Supplementary Fig. 10d,e). In contrast, laser fluence E2 caused graphitization from the amorphous SiC layer (~17 nm) through sublimation of Si element (Supplementary Fig. 10f), C nucleation (Supplementary Fig. 10g), formation of multilayer graphene (Supplementary Fig. 10h), in sequence, by increasing the number of laser pulses up to several hundreds of irradiations. On the other hand, thin phase-separated C and Si layers were observed by using high laser fluence of E3 (Supplementary Fig. 10c).

From the experimental results, we have found required conditions for the phase separation as followings: (1) solid-state binary material should include one element that has the lowest surface energy from liquid state of binary system. (2) The one element should have a larger melting temperature than both the other element and binary compound. For this reason, compound material, which includes carbon, has a high possibility for a phase separation. (3) A wide bandgap compound materials are good candidates due to their characteristic of semi-insulator. (4) We have to avoid melt-mediated amorphous phase transition via quenching, instead of the phase separation, which is mainly related to pulse duration and energy density of laser.

In conclusion, we demonstrate that a single-pulse irradiation induces melt-mediated phase separation into C and Si layers on SiC surface by characterization with HRTEM and TRR analysis. MD simulations indicate that the graphitic C layer is formed by minimization of surface energy from liquid SiC. Additional pulses lead to the selective sublimation of elemental Si from the phase-separated layers due to the different melting temperatures of the two elements. Therefore, our results give indication of synthesizing ultra-thin nanomaterials through the laser-induced phase separation of a binary system.

Methods
Sample preparation and laser irradiation. 4H-SiC wafers with low doping (n = 2.2 × 10¹⁸ cm⁻³) and chemical mechanical polishing were purchased from Cree. Specimens, 5 × 6 mm², were cut from the wafers and cleaned by sequential ultrasonic baths in acetone, isopropyl alcohol and deionized water to remove...
after cleaning, a SiC substrate was placed into a heating stage (Linkam, TS1500). This is a small chamber (100 × 100 mm²) that enables the bottom of the substrate to be heated up to 1,000 °C with inert gas supply. The sample was annealed at 650 °C for surface cleaning and it was maintained at the same temperature during laser irradiation in an Ar flow. The laser system used is comprised of a XeCl excimer laser (Coherent, LPX model, λ = 308 nm, pulse duration ~30 ns) and beam delivery optics with a homogenizer optical system. The laser beam is concentrated 5 × by a projection lens of 11 × 11 mm² and 430 μm in diameter. Each pulse had a laser fluence of 1.653 mJ cm⁻² and a repetition rate of 1 Hz. For multi-pulse irradiations over 100 pulses, 5 Hz was used to reduce the processing time. Both repetition rates appeared to have the same effect because the heating and cooling processes are determined by the nanosecond laser pulse width. All the laser experiments were performed with the same substrate and experimental conditions except for the number of pulses.

**TEM analysis.** To prepare cross-sectional TEM samples of the 4H-SiC, we used a focused ion beam milling technique (FEI, Helios 450XPi). A Pt metal layer was deposited to protect the surface of the sample before milling. To make much thinner and undamaged TEM samples, we additionally milled the samples using a low-energy Ar-ion milling system (Fischione Model 1040 Nanomill). To structurally characterize the top surface, we acquired atomic resolution TEM images using a spherical aberration-corrected TEM (FEI Titan3 G2 60-300 with an image-forming Cs corrector at 300 kV) because C-based materials can be easily damaged by high-energy electron beam irradiations. EFTEM elemental mapping and EELS spectra were recorded using a Gatan Imaging Filter (Gatan Quantum 965 ER). EELS spectra were collected in the STEM mode using a dispersion of 0.25 eV per channel and a 2.5 mm aperture. The elemental mapping was acquired with the three-window method.

**Numerical simulation.** The numerical simulation performed in this study is widely used for the analysis of the thermal behaviour of laser–solid interactions involving heat generation and cooling at the surface of the irradiated area by light absorption. The thermal simulation parameters of SiC were utilized with [720/(T−695)] of thermal conductivity and cooling (1.12 × ln (T)−4) of latent heat capacity which are determined from previous studies. In addition, values of the real part n(2.9) and imaginary part k(0.1) of the refractive index as optical parameters were used for a 308 nm wavelength. The laser intensity as a function of time of our 308 nm XeCl laser (Supplementary Fig. 6B) and optimized experimental conditions (that is, fluence and substrate heating) were used to investigate the temperature history of the SiC surface during a short pulse (30 ns).

**Measurement of TRR signal and laser intensity as a function of time.** The TRR system is illustrated in Supplementary Fig. 6A. It consists of two photodetectors (Thorlabs, DET10A), a filter (Thorlabs, FEL0500), a probing laser diode (635 nm) and an oscilloscope (Tektronix, TDS5054). The TRR method is used to detect changes in the laser diode signal during 308 nm laser irradiation of the sample surface because semiconductor materials such as Si and SiC have a higher reflectance in the liquid phase that is maintained longer than the time of the laser pulse. For this reason, the principle of TRR analysis uses different reflectances of material in the solid and liquid phases. One photodetector is for detection of the reflectance from the SiC surface. Generally, the photodetector can monitor a wide range of wavelengths, from 200 to 1,100 nm. Therefore, a filter is combined with the photodetector and serves the important role of blocking the signal of the 308 nm laser because we are interested in only information from the sample surface (here, liquid phase of SiC). The other photodetector detects the 308 nm signal of the laser beam. The two detectors are combined with an oscilloscope. The 308 nm XeCl laser has a unique intensity variation as a function of time with three humps (peaks), which were measured by a photodetector with an oscilloscope (Supplementary Fig. 6B). Normally, the pulse duration (full width of half maximum) is considered to be ~30 ns, which is only for the first hump. In this study, the second hump causes accumulation of thermal energy with the first hump, resulting in the highest surface temperature (Supplementary Fig. 4) and reflectance signals (Figs 3 and 4d) at 75 ns.

**Calculation of atomic volume ratio of Si and C.** To evaluate the atomic volume ratio of Si to C, we carried out density functional theory (DFT) calculations using the Vienna Ab-initio Software Package programme. All DFT computations were performed using a plane-wave basis set and the Perdew–Burke–Ernzerhof exchange-correlation functional coupled with an empirical van der Waals correction (PBE-vdW) to provide a good description of the London dispersion forces between Si atoms and SiC. A Si-terminated 2×2×1 supercell of [111] and [121] unit cells, consisting of 40 atoms, was used for the Si crystal and graphite unit cells, respectively, and an energy cutoff of 600 eV was considered for the plane-wave basis set. After optimizing the unit cells of cubic Si with the diamond structure and graphite, we found that the atomic volume ratio is ~1.2 for graphite C and cubic Si (8.75 versus 19.75 Å³ per atom). All details for the optimized structures, including the number of atoms, lattice parameters and volumes are listed in Supplementary Table 1 (ref. 28).

**MD simulation.** It has been widely discussed that the direct simulation of the solidification process is hardly available using conventional MD simulations while the simulation of melting process is possible. It is still ambiguous how the laser heat energy can be incorporated in MD simulations, albeit there are several attempts. Instead of performing a direct MD simulation for the overall process, we built 10 different structures modelling the initial, intermediate and final states of the phase separation process: (Model 1) initial solid state of SiC (SiC (s)) is built using a Si-terminated 3C-SiC (111) slab model (Supplementary Fig. 3), because the graphic layers are observed to be grown on top of 3C-SiC (111) layers. The lateral dimension of the slab model is a 5x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C). The lateral dimension of the slab model is a 5√3x3x2a unit cell, where the lattice parameter of a is 4.34 Å (chosen from DFT result), consisting of 40 bilayers (4,800 Si and 4,800 C).

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Author contributions
I.C., H.Y.J., S.-Y.C. and K.J.L. designed the project and analysed the whole data; I.C. performed the laser experiments, analysed TRR signals, performed numerical simulation and obtained Raman data; H.Y.J. performed TEM and EELS analyses; H.S., G.K. and H.K. performed MD simulations, DFT simulations and calculation of atomic volume ratio; A.M.C. carried out measurement of TRR signals; J.S.I. contributed to the numerical simulation and analysis of melt-mediated phase separation; I.C., H.Y.J., H.S., G.K., H.K., S.-Y.C. and K.J.L. co-wrote the manuscript; M.B. and R.S.R. discussed results and revised the manuscript; K.J.L. and S.-Y.C. are responsible for managing all aspects of this study including the writing of manuscript.

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SUPPLEMENTARY FIGURES

**Supplementary Figure 1** | HRTEM image of a single-pulse irradiated 4H-SiC surface. FFT patterns clearly show a (111)-oriented 3C-SiC layer and an (0001)-oriented 4H-SiC substrate. Scale bar = 5 nm.
Supplementary Figure 2 | Side view of the Si-face of a (111)-oriented 3C-SiC substrate. Gray and yellow spheres represent C and Si atoms, respectively. The periodic boundary condition box is shown as a blue solid line.
Supplementary Figure 3 | Potential energy plot for the formation process of multilayer graphene from the SiC system. Each step is optimized by performing MD simulation and the insets show the side view of each step taken from the MD simulations. All simulation details are described in the “Molecular dynamics simulation” section. After SiC (s) is transformed into SiC (l) by the high-energy laser source corresponding to thermal treatment up to approximately 3500 K, it reaches a metastable state with surface graphene layers. During this process, C atoms are extracted from the SiC (l) surface and are converted into a multilayer graphene structure by decreasing the overall potential energy of SiC (l) layer atoms. In other words, the potential energy reduction induces a thermodynamic driving force to generate graphitic C layers from the SiC (l) surface and to consequently reach the metastable state. Gr indicates one layer of carbon (graphene).
Supplementary Figure 4 | Temperature distributions for a 4H-SiC surface irradiated with a single-pulse by one-dimensional numerical simulation. Simulated temperatures were investigated in various positions of surface, 50, 100, 200, 300, 500, and 1000 nm. There are very similar temperatures from the top surface to a depth of 50 nm due to the high thermal conductivity of single-crystal SiC. The surface temperature was increased to 2784 K by the first hump of laser beam, which is below the melting point of SiC. The second hump of laser beam leads to an accumulation of thermal energy and the surface temperature increases to 3541 K at 75 ns. This simulated temperature indicates that laser fluence supplies enough thermal energy to melt the SiC surface.
Supplementary Figure 5 | Atomic potential energy spectra of the simulation systems optimized by performing MD simulations. The color spectrum bar in the right-top indicates the relative potential energy referenced to the energies of bulk atoms. Red and blue colors describe a high potential energy regime and a low potential energy regime, respectively. After SiC (s) is transformed into SiC (l) by a high-energy laser source, the surface atoms arrange themselves into graphene which reduces the surface potential energy. Eventually, the surface potential energy reduction by graphitic C layer formation induces a thermodynamic driving force to reach the metastable state even though the potential energy of the residual atoms in SiC_{1-x} (l) below the surface graphene layers remains high. Gr indicates one layer of carbon (graphene).
Supplementary Figure 6 | (a) Schematic of the measurement system of time-resolved reflectance analysis (b) Laser intensity as a function of time (laser temporal) of 308 nm XeCl excimer laser (Coherent, LPX model). Single-pulse was measured by using photo detector and oscilloscope.
Supplementary Figure 7 | (a) HRTEM image of a non-uniform area on 4H-SiC surface after two irradiation pulses. Scale bar = 10 nm. (b) Magnified image of white-dotted rectangle area in a. Scale bar = 5 nm. (c, d) EFTEM mapping images of C K- and Si L-edge. Scale bars = 10 nm.
Supplementary Figure 8 | HRTEM images of 4H-SiC surface after 30 (a), 100 (b), and 300 (c) irradiation pulses. Scale bars = 2 nm. Double-sided arrows indicate 3C-SiC layers. (d) Raman spectra of laser-induced multilayer graphene on 4H-SiC surfaces after irradiation of 30 (black line), 100 (red line), 200 (blue line), and 300 pulses (green line). Three representative peaks, including the defect-induced D peak, in-plane vibrational G peak, and two phonon scattered 2D peak are clearly observed at 1364, 1583, and 2720 cm\(^{-1}\), respectively. The inset shows magnification of 2D peak. The gray line is the Raman spectrum for an original 4H-SiC substrate as a reference.
Supplementary Figure 9 | EELS spectra of C layers formed by multi-pulse irradiation. Both data of ten and one hundred irradiations show a highly graphitic ordered structure which is comparable to CVD-grown multilayer graphene.
Supplementary Figure 10 | Investigation of laser-SiC interaction as a function of laser fluence and the number of irradiation pulses. HRTEM images of 4H-SiC surface after single-pulse irradiation with laser
fluence of 1000 (a), 1200 (b), and 1653 mJ cm\(^{-2}\) (c). HRTEM images of 4H-SiC surface after 50 (d) and 600 (e) irradiation pulses with laser fluence of 1000 mJ cm\(^{-2}\). HRTEM images of 4H-SiC surface after 200 (f), 400 (g), and 600 (h) irradiation pulses with laser fluence of 1200 mJ cm\(^{-2}\). Scale bars = 5 nm. Our study indicates two different mechanism with melt-mediated phase separation or amorphous phase transition for the formation of C layer on single-crystal SiC surface, compared to the conventional thermal decomposition\(^{16-18}\) and 248 nm KrF laser irradiation\(^{19}\). We estimate that 308 nm XeCl laser has a higher possibility to melt SiC surface due to its longer pulse duration (which includes the second hump at laser intensity, Supplementary Fig. 6b) and a higher absorption depth at 308 nm wavelength, compared to effects of 248 nm KrF laser\(^{19}\).
SUPPLEMENTARY TABLE

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**Supplementary Table 1** | The number of atoms, lattice parameters, and volumes for each unit cell after geometry optimization steps.
**SUPPLEMENTARY NOTES**

**Supplementary Note 1**

**Time-resolved reflectance analysis of single-pulse irradiation:** We divided the time-resolved reflectance (TRR) signal into six different regions corresponding to observed signal changes to analyze the phase separation and surface reconstructions of single-crystal SiC. The first region indicates the lowest reflectance of 4H-SiC surface before laser irradiation. The intensity of reflectance at 37 ns (the second region) was slightly increased, which corresponds to the hot solid state (before melting) by irradiation of the first hump of laser beam. The third region was determined from 50 to 180 ns including a peculiar shape at 75 ns. The TRR signal was remarkably increased from 50 to 75 ns by supplying the second hump of laser pulse, indicating melting of 4H-SiC. The unusual high intensity at 75 ns is estimated to include the reflectance signals from the 4H-SiC surface and the laser intensity. Phase separation was considered to be produced before complete solidification of the liquid SiC layer in the third region. The thicknesses of the melt-mediated phase separation region (~7.5 nm) and the transition layer (3C-SiC, ~15 nm) were very thin, compared to the heat diffusion length (~1 um) estimated from the heat transfer equation, $\sqrt{2D\tau}^{22,23,27}$. Therefore, thickness up to several hundreds of nanometers could be melted and recrystallized to 4H-SiC, whereas only a thin layer (~15 nm) under the separated layer was transformed to 3C-SiC which is a stable phase in non-equilibrium conditions. A long flattened region was observed from 180 to 450 ns (fourth region), which demonstrates the existence of a liquid phase. The TRR signal of the fifth region, showing the final signal change, between 450 and 480 ns shows solidification indicating the coexistence of liquid and solid phases. This solidification process only involves Si due to its low melting temperature (~1700 K), compared to that of SiC (~3100 K). The TRR signal of the sixth region after 480 ns is very stable, which means complete cooling of surface.

**Supplementary Note 2**
**TRR analysis of the second irradiation pulse:** We analyzed melt-mediated surface reconstructions with six different regions corresponding to changes of the TRR signal. The reflectance of the first region indicates a graphitic C surface before the second irradiation pulse. The first hump of laser beam caused a remarkable increase of reflectivity at 37 ns, unlike the small increase in the single-pulse irradiation at the same time (Fig. 1g). This is related to the initial surface structure of graphitic C/poly-Si/3C-SiC on 4H-SiC. The poly-Si layer was melted and evaporated as soon as irradiation of the first hump of laser beam. The third region corresponding to a decrease in the TRR signal was determined to be from 50 to 150 ns. Similar to the results for the single-pulse irradiation, an unusually high intensity was observed at 75 ns by supplying the second hump of laser beam. Both 3C-SiC and 4H-SiC were molten at this time. A flattened region indicating a liquid phase between 150 and 290 ns (the fourth region) is much shorter than for the single-pulse irradiation, as shown in Fig. 1g. On the other hand, this flattened region indicates liquid SiC because a separated Si layer was not detected on the surface, as shown in Fig. 4b. The TRR signal of the fifth region between 290 and 320 ns presents solidification indicating coexistence of liquid and solid phases of SiC. After 320 ns (the sixth region), the TRR signal was stable, which means complete cooling of the surface. The intensity of the TRR signal during the six regions was very similar to that of the first region, because both regions indicate the existence of the same C material on the surface before and after the second irradiation pulse, which is in agreement with the HRTEM analyses.

**Supplementary Note 3**

**TRR analysis of multi-pulse irradiation:** The TRR signal for the 4H-SiC surface irradiated with third pulse shows a very similar spectrum shape to that of the second irradiation pulse. This means that there was no further generation of a Si layer by phase separation. Additional TRR data from 20 to 100th pulse show a similar spectrum shape including the flattened period. Therefore, the thickness increase of the C layer is believed to occur by the addition of C atoms from the interface between the bottom C layer and the liquid SiC surface through laser-induced melt-mediated decomposition of SiC.