INTRODUCTION

Graphene, an atomically thin two-dimensional (2D) sheet of covalently bonded carbon atoms, presents new opportunities in fundamental research and practical applications (1), due to its unusual electronic (2), optical (3), thermal (4), and mechanical properties (5). Large-area high-quality graphene growth has been intensively studied, and significant advances have been made toward practical device application of graphene (6–9). Among the options for graphene synthesis, chemical vapor deposition (CVD) can yield high-quality, polycrystalline single-layer graphene on catalytic substrates such as Cu (7). Typically, CVD growth yields a polycrystalline graphene structure with grain sizes in the order of a few hundred nanometers (10), a few micrometers (11), or even a few hundred micrometers (12). Grain boundaries represent defects in the graphene lattice, because they typically deviate from the ideal honeycomb structure. Grain boundaries occur when graphene domains nucleate simultaneously at different locations on the growth substrate and then coalesce. In addition to these dislocation-like line defects, point defects (such as Stone-Wales defects, adatoms, vacancies, or substitutional impurities) are observed (13, 14). Moreover, the transfer of graphene from the growth substrate to a target substrate, typically a silicon dioxide (SiO₂) surface of a silicon (Si) substrate, introduces wrinkles (15), folds (16), and cracks (17) in CVD graphene. In particular, the form and distribution of grain boundaries are critically affecting the electrical, thermal, mechanical, and chemical properties of the graphene, with smaller grain sizes potentially reducing electronic mobility (6), lowering thermal conductivity (18), and reducing ultimate mechanical strength (19). However, defects, such as grain boundaries, might be beneficially exploited by controlled grain boundary engineering (20). Thus, the study of grain boundaries in graphene is important for graphene characterization, for understanding the characteristic behavior of graphene in specific device applications, and for optimizing graphene growth conditions. A number of reports demonstrate methods for characterizing graphene grain boundaries using transmission electron microscopy, scanning tunneling microscopy, or atomic force microscopy (AFM) (10, 11, 21, 22). Although these techniques can obtain atomic resolution at graphene grain boundaries, they can be time-consuming and have limited capabilities in accessing large-scale information about the distribution of the grain boundaries. By contrast, techniques using optical microscopy (23–27), 2D Raman imaging of the integrated intensities of the G and D peaks (28), or scanning electron microscopy (SEM) imaging of transition metal dichalcogenides that are epitaxially grown on graphene (29) are in principle suitable for characterizing graphene grain boundaries at larger scales. For instance, graphene grain boundaries have been visualized using optical birefringence in graphene covered by a liquid crystal (23). Graphene grain boundaries have also been visualized in graphene grown on a copper foil using optical microscopy, by selectively oxidizing the underlying copper foil through the grain boundaries in a moisture-rich atmosphere combined with ultraviolet irradiation (24), by selectively oxidizing the copper through the grain boundaries by electron injection from an etching process using a sodium chloride solution (25), by selectively oxidizing the copper in between grains of partially CVD grown graphene using a thermal annealing process (26), and by selectively etching the graphene grain boundaries in oxygen plasma and subsequently oxidizing the underlying copper by thermal heating (27). However, these techniques are either very elaborate or require the graphene to be placed on a copper substrate. Different characterization methods for observation of CVD graphene grain boundaries are summarized in table S1. Here, we propose a simple method for visualizing grain boundaries in graphene placed on a SiO₂ substrate with optical microscopy, SEM, or Raman spectroscopy. The method requires the exposure of the graphene to vapor hydrofluoric acid (VHF) before imaging (Fig. 1A), thereby partially etching the SiO₂ underneath the graphene by diffusion of the VHF through the graphene grain boundaries. Thus, our approach allows for efficient and rapid large-scale visualization of graphene grain boundaries. As many graphene device applications are achieved using CVD graphene that is transferred from the growth substrate (for example, a copper foil) onto a SiO₂ surface, the proposed metrology is highly relevant for the development, optimization, and understanding of polycrystalline graphene targeted at these types of applications.
RESULTS AND DISCUSSION

Experiments were conducted using CVD-grown graphene on a copper foil (Graphenea) that was transferred onto 125-nm-thick SiO2 layers on Si substrates using a wet transfer method (see Materials and Methods) (30). At this state, graphene grain boundaries are not visible using optical microscopy, SEM, or Raman spectroscopy because of the nanoscale dimensions of the line defects (Fig. 1, B and F) (24). After the graphene on the SiO2 surface is exposed to VHF at 40°C for different time periods (30, 60, and 120 s), line patterns in the areas covered by the graphene become visible in both optical microscopy images (Fig. 1, C to E) and SEM images (Fig. 1, G to I). These line patterns become more distinct and increase in number with increasing time of exposure to VHF. When the time of exposure to VHF is extended from 30 to 60 s, more line patterns can be observed using optical microscope and SEM imaging (Fig. 1, C, D, G, and H). Upon further increasing the exposure time to VHF from 60 to 120 s, the density of the line patterns does not increase (Fig. 1, F and I), whereas the existing line patterns get more pronounced, that is, the lines get wider. The CVD graphene used in our experiments has a polycrystalline graphene structure with grain sizes in the order of a few micrometers. The optical microscope and SEM images in Fig. 1 show that the dimensions of the areas surrounded by the line patterns are in the range of a few micrometers, which indicates that the line patterns are likely caused by, and represent, the grain boundaries in the graphene.

To further demonstrate that the line patterns correspond to the grain boundaries of CVD graphene, the same type of CVD graphene on copper that was used in our VHF exposure experiments was characterized by low-energy electron microscopy (LEEM) and low-energy electron diffraction (LEED). The LEED pattern (Fig. 2A) shows the presence of multiple rotated graphene domains on various facets of the copper foil surface, similar to what has been reported previously (31). By successively selecting single diffraction spots for imaging (dark-field LEEM), the lateral distribution of domains becomes visible (Fig. 2B). The observed grain sizes range from ~2 to ~10 μm. Both the grain pattern and the dimensions are consistent with the observed patterns and dimensions visualized by our method. This further indicates that the line patterns in our method are mainly attributed to the grain boundaries of CVD graphene. We have also attempted to characterize graphene samples placed on a SiO2 surface with LEEM and LEED; however, it was not possible to obtain reasonable LEED patterns for aligning the instrument. This could be due to residues on the transferred graphene (for example, from the supporting layer necessary for transfer) as the method is highly surface-sensitive because of the short mean free path of electrons at the energies used for LEED.

Beside the line patterns, in the SEM images, we observed a gradual change of the surface morphology in the areas surrounded by the line patterns upon exposure to VHF (fig. S1). In these areas, corrugations with a characteristic size of 50 to 100 nm in-plane were formed across the surface of the samples (fig. S1). The SiO2 surface areas that had not been covered by graphene show very similar corrugations after exposure to VHF, whereas no line patterns appear in these areas (fig. S2). The evolution of the surface morphologies in the areas in between the line patterns (the grain areas) that depend on the time of exposure to VHF illustrates that the reaction of VHF with the SiO2 substrate underneath the graphene is initiated near the graphene grain boundaries and spreads from there across the graphene crystallites. To verify the stability and repeatability of our proposed method, different graphene samples were prepared, and very similar phenomena were observed. For instance, graphene transferred to different Si substrates containing...
1.4-μm-thick SiO₂ surface layers were exposed to VHF for 60 and 120 s, respectively (Fig. S3), which resulted in a comparable line pattern. In addition, single-layer graphene was transferred directly to a Si substrate covered only by a native SiO₂ layer (~1 nm thick) and exposed to VHF for 60 and 120 s, respectively (Fig. S3). Line patterns with similar dimensions and structure as in the experiments with the thick SiO₂ layers were observed; however, the line patterns in the case of the native SiO₂ are much less pronounced and not uniformly distributed. The results from these control experiments show that the presence of a SiO₂ layer of sufficient thickness underneath the graphene is critical for creating pronounced line patterns after exposure to VHF.

The quality of the transferred graphene on SiO₂ was characterized by scanning micro-Raman spectroscopy before and after exposure of the graphene to VHF for different exposure times of 0, 30, 60, and 120 s (Fig. 3). The absence of an appreciable D peak (1350 cm⁻¹) shows relatively high-quality single-layer graphene before exposure to VHF (Fig. 3A). Note that the Raman spectrum in Fig. 3 (A4) is obtained on a monolayer region (Fig. 3A2), whereas the Raman spectrum in Fig. 3 (A3) is obtained on a multilayer region (Fig. 3A2), thereby having a markedly lower intensity ratio of the 2D and G peaks (I₂D/I_G). After exposure to VHF for 30 s, there is still an obvious G and 2D band, both on the line patterns and in between the line patterns (within the grains) (Fig. 3B). This can be explained by the fact that the width of the line patterns created during VHF exposure for 30 s is smaller than the diameter of the Raman laser spot (~300 nm) that is represented by the blue and purple circles in Fig. 3 (A2, B2, C2, and D2). Thus, the laser beam reaches across the line, thereby at the same time characterizing the graphene on the line patterns and beside the line patterns. After exposure to VHF for 60 and 120 s, the line patterns are found to widen, and the G and 2D bands weaken substantially at the line patterns. By contrast, the G and 2D bands remain in the areas between the line patterns (Fig. 3, C and D). The treatment of graphene in fluorine-containing atmospheres (for example, F₂ and XeF₂) has been shown to result in fluorinated graphene (32–36), and an evolution of the Raman spectra similar to the one we saw in our experiments (Fig. 3) was reported upon fluorination of graphene and graphite in gaseous atmospheres of XeF₂ and F₂ after several weeks of exposure to these gases (33, 34). The disappearance of characteristic peaks at the line patterns (Fig. 3D3) may be explained as follows: Because of the enhanced chemical reactivity of graphene at grain boundaries (27, 37, 38), fluorination preferentially occurs at these sites, thereby opening a relatively wide band gap in the energy spectrum of the graphene (34). An increase of the time of exposure to VHF leads to an increase in the degree of fluorination of the samples, thereby increasing the band gap (Fig. 3, B3, C3, and D3). As shown in Fig. 3 (D3), when the width of the band gap of the graphene at the grain boundaries is larger than the excitation photon energy of the Raman spectrometer (here, λ = 532 nm), the fluorinated graphene at the grain boundaries acts like a wide-band gap semiconductor and becomes transparent for the excitation radiation of the Raman tool laser (34). In addition, cracks may form at the graphene grain boundaries after exposure to VHF that can lead to decreased or vanished intensities of the characteristic peaks of the Raman signals. Energy-dispersive x-ray (EDX) analysis was carried out on the graphene after VHF exposure. Although fluorine sometimes appears in the EDX spectra, the results are not conclusive due to the low fluorine content and the low detection sensitivity of EDX. The Raman spectroscopy maps in Fig. 3 (A, B, C, and D) are not obtained from the same position of graphene before and after VHF exposure, but from four different samples accordingly, where VHF time is varied systematically for a clear comparison. The ambiguous line patterns in Fig. 3 (A1) are likely wrinkles, resulting from the graphene transfer, and therefore do not correspond to the etched lines in Fig. 3 (B1, C1, and D1) at all.

The microscopic features defining the line patterns in our samples were correlated with nanoscale information using AFM imaging before and after exposing the samples to VHF (Fig. 4). Before exposure to VHF, no topographical features can be observed in the transferred graphene layers on the SiO₂ substrate surface (Fig. 4, A and B). When the VHF exposure time was 30, 60, and 120 s, obvious topographic features outlining the line patterns start appearing with heights on the order of 15 to 20 nm (Fig. 4, C and D), 25 to 40 nm (Fig. 4, E and F), and 70 to 80 nm (Fig. 4, G and H), respectively. These topographic features in the SiO₂ layer below the graphene are resulting from the exposure to...
VHF and they are the reason why the line patterns can be easily observed with optical microscope and SEM imaging as shown in Fig. 1.

In addition to the structural investigations, we have carried out four-point probe sheet resistance measurements of graphene placed on a 125-nm-thick SiO2 layer before and after exposure to VHF to monitor the electrical properties of the graphene. The dependence of the graphene sheet resistance on the time of exposure to VHF is plotted in fig. S4. The sheet resistance of the graphene before exposure to VHF is in the range from 1 to 1.5 kilohm/sq and in the range from 1.5 to 5 kilohm/sq after exposure to VHF for less than 30 s. Thereafter, the sheet resistance increases sharply by six orders of magnitude after exposure to VHF for 60 s, with an additional sheet resistance increase by three orders of magnitude after exposure to VHF for 120 s. This sharp increase of the sheet resistance from ~10^3 to ~10^12 ohm/sq indicates the gradual formation of insulating regions (34, 39), possibly due to the fluorination of graphene and/or the formation of cracks at the graphene grain boundaries after exposure to VHF for more than 15 s and up to 120 s, which is in good agreement with the results of the Raman spectroscopy experiments (Fig. 3). Similar resistance changes were observed for graphene placed on a 1.4-μm-thick layer of SiO2 after exposure to VHF (fig. S4). In another experiment, after exposure to VHF, the graphene was removed from the surface of several samples by an O2 plasma etching process (1 min at 80 W with 80 sccm O2 at 80 mtorr pressure), followed by 30 min in Piranha solution to remove residues from the sample. This allowed a detailed investigation of the topography of the underlying SiO2 substrate surface. Unexpectedly, the AFM topographic images show that the surface of the line patterns outlining the graphene grain boundaries are at a higher level than the surfaces of the areas previously covered by pristine graphene crystallites, that is, the areas between the line patterns (Fig. 4I). The surfaces of the line patterns are at the same level as the SiO2 surfaces that were not covered by graphene during VHF etching. This means

**Fig. 3. Raman characterization.** Raman spectroscopy map of graphene placed on a SiO2 surface before exposure to VHF (A): (A1) map of the intensities of the 2D band. (A2) is a close-up of (A1). (A3) and (A4) are Raman spectra of two areas in (A2), respectively. The corresponding data after VHF exposure for 30, 60, and 120 s, respectively, are displayed in (B) to (D). CCD, charge-coupled device.
that the etching rate of SiO₂ in areas that are not covered by graphene is identical with the etching rate of the SiO₂ at the line patterns (that is, the graphene grain boundaries). Surprisingly, the etching rate of the SiO₂ underneath the graphene crystallites (that is, the areas in between the graphene grain boundaries) is higher than the etching rate of both the SiO₂ directly exposed to the VHF and the SiO₂ at the line patterns. A similar observation of an increased etching rate of SiO₂ underneath mechanically exfoliated graphene was reported by Stolyarova et al. (40). Our experiments demonstrate that the visibility of the line patterns in areas covered by graphene is caused by a differential etching of the underlying SiO₂ during exposure to VHF. A similar process of differential VHF etching of SiO₂ around individual carbon nanotubes (CNTs) has been reported previously for visualizing CNTs with optical microscopy (41). Here, we provide a possible explanation concerning the processes involved in forming the line patterns underneath the graphene (Fig. 5A): First, VHF along with water molecules evaporates from the liquid HF solution and preferentially interact with the graphene grain boundaries due to their enhanced chemical reactivity (27, 37, 38), thereby forming open channels through which molecules can diffuse. Next, water condenses at the surfaces, and dissolved HF interacts with the graphene and the SiO₂ underneath the graphene grain boundaries. Although etching of SiO₂ with VHF is a

Fig. 4. AFM characterization. (A) AFM image of the surface topography of graphene placed on a SiO₂ substrate surface before exposure to VHF. (B) Height profile of the selected area in (A). The corresponding data after VHF exposure for 30, 60, and 120 s, respectively, are displayed in (C) to (H). (I) AFM characterization of a SiO₂ surface that has been covered with graphene and a SiO₂ surface that has not been covered with graphene while exposed to VHF. AFM data were taken after exposure of the sample to VHF for 120 s, O₂ plasma etching for 60 s at 80 W with 80 sccm of O₂ at 80 mtorr, and piranha cleaning for 30 min. (I1) Optical microscope image of the SiO₂ surfaces after the etching and cleaning procedure. (I2) AFM image of the surface topography of the SiO₂ surfaces after the etching and cleaning procedures. (I3) Height profile of the selected area in (I2), spanning SiO₂ surfaces that were covered and that were not covered by graphene while exposed to VHF. (I4) and (I5) show an AFM image and a height profile of a SiO₂ surface that was not covered by graphene while exposed to VHF.

very complex process with numerous sequential equilibrium reactions (42, 43), a simple illustration of the net reactions shows that an excess of H₂O molecules is produced during the etching reaction (see Materials and Methods)

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4
\]  

(1)

\[
\text{Si(OH)}_4 + 4\text{HF} \rightarrow \text{SiF}_4 \uparrow + 4\text{H}_2\text{O}
\]  

(2)

The SiO₂ etch rate in HF is intimately linked to the presence of water (40, 41, 43). Thus, SiO₂ etching in a low water concentration environment, such as SiO₂ that is directly exposed to HF vapor (that is, the cases of SiO₂ that is not covered with graphene and SiO₂ in the areas of the graphene grain boundaries), will be slower than etching of SiO₂ that is exposed to liquid water with dissolved HF (that is, the case of the areas beneath the graphene crystallites in between the line patterns, provided that there is an efficient feed of HF to the water reservoir underneath the graphene) (40). We speculate that VHF diffusing through the graphene grain boundaries is absorbed by the water trapped underneath the

Fig. 5. Proposed etching mechanism during exposure to VHF. (A) Schematics of the proposed reaction processes when exposing graphene that is placed on a SiO₂ substrate surface to VHF. (B) SEM micrograph of a SiO₂ substrate surface that is covered by grains of CVD-grown graphene that are not fully grown to a sufficiently large size to completely connect to neighboring grains, before exposure to VHF (blue lines around grains added for clarity). Thus, the grain boundary regions can be identified in the areas where the blue lines of neighboring grains merge. (C) SEM micrograph of the sample shown in (B) after exposure to VHF for 17 s at room temperature and subsequent 13 s at 40°C. The SEM micrographs of (B) and (C) are taken from the same chip but not exactly from the same position.
graphene in the regions between the grain boundaries, thereby efficiently transferring HF molecules across the graphene grain boundaries to the liquid water reservoirs trapped underneath the graphene crystallites, thereby effectively realizing liquid water reservoirs with dissolved HF (Fig. 5A). In this manner, higher etch rates are achieved underneath the graphene crystallites as compared to the SiO2 areas that are directly exposed to VHF and in which the etch rate depends on the water condensation rate. The etch rates of the SiO2 used in our experiments when exposed to VHF or liquid HF have been measured and support the above hypothesis. That is, SiO2 was etched in VHF (that is evaporated from a 25% liquid HF solution) or in 10% liquid HF, with extracted etch rates of 45 and 80 nm/min, respectively. This confirms the lower etch rates of SiO2 in VHF than in liquid HF solutions with comparably low concentrations.

Graphene grain boundaries are typically formed during the growth process by the joining of adjacent graphene islands initiated by separate nucleation seeds (44). To further verify our proposition that the graphene grain boundaries are predominant for the reaction with VHF in forming the visible line patterns, we have used CVD graphene samples where the growth time for the graphene was set to obtain partially isolated single grains of graphene. After transfer, the grains thus only partially cover the surface of the chip substrate. In these samples, the graphene grain boundaries can be distinguished between different grains (Fig. 5B). After exposing these samples to VHF, the line patterns predominantly appear at the locations of grain boundaries surrounding grains where a grain merges with a neighboring grain (Fig. 5C and fig. S5). This is expected and consistent with the other experimental results. To evaluate what happens when double-layer graphene is present on the SiO2 surface instead of single-layer graphene, we exposed manually stacked double-layer CVD graphene transferred onto a SiO2 substrate surface to VHF for 120 s under the same conditions as the single-layer graphene. In these experiments, line patterns can still be observed by optical microscope and SEM imaging in selected areas (fig. S6), but the effect is significantly less pronounced than in single-layer graphene. This is expected because effective diffusion of VHF may happen only in areas where one of the stacked graphene layers is defective. Finally, a control experiment was performed in which single-layer graphene placed on a SiO2 substrate surface was immersed in 5% liquid HF at room temperature for 60, 120, 180, and 240 s, respectively. In these experiments, we did not observe the characteristic line patterns after HF exposure. By contrast, in these experiments the graphene was destroyed or lifted off the SiO2 surface during immersion in the liquid HF (fig. S7). This confirms that the proposed method for large-area imaging of graphene grain boundaries relies on the specific chemical reactions that occur when exposing graphene on a SiO2 surface to VHF.

Together, we have demonstrated a fast and simple method for large-area visualization of grain boundaries in CVD graphene transferred to a SiO2 surface. We used indirect evidence from different characterization approaches along with control measurements, all yielding consistent results supporting the proposition that our method visualizes grain boundaries in CVD graphene. The method only requires VHF etching and optical microscope inspection, which both are standard processes in wafer fabs, and thus, the method can be applied in these environments without additional investment. Note that our method is invasive; that is, the graphene and the substrate are modified during grain boundary visualization, which is in contrast to noninvasive grain boundary visualization methods, such as Raman spectroscopy (28), in which the graphene sample is not modified (see table S1). However, despite its invasiveness, our method has the clear benefits of simplicity, high speed, and throughput. Thus, this method could be very useful to speed up the process of developing large-scale high-quality graphene synthesis because it offers a quick evaluation of the grain boundary density on large-area graphene samples. It can also be used for postmortem analysis of emerging graphene devices that use graphene patches placed on a SiO2 substrate, such as graphene-based pressure sensors, transistors, and gas sensors, to study the effects of grain boundary line defects on device performance.

CONCLUSION

In conclusion, we report a fast and simple methodology for large-area visualization of grain boundaries in CVD-grown graphene using optical microscopy, SEM imaging, and Raman spectroscopy. Our methodology relies on the differential etching behavior of SiO2 near graphene grain boundaries and of SiO2 placed underneath graphene crystallites upon exposure to VHF. We attribute the observed realization of visible line patterns to higher SiO2 etch rates in the areas covered by the grains. This can be explained by a more efficient etching of SiO2 caused by reservoirs containing liquid H2O with dissolved HF underneath the graphene grains as compared to the areas in vicinity of the grain boundaries that do not contain trapped liquid H2O. The resulting topographical differences and, hence, the grain boundaries can thus be easily observed visually on a microscopic scale. The proposed approach is specifically attractive for rapid and large-scale imaging of graphene grain boundaries during development and monitoring of graphene growth processes, ultimately contributing to improved understanding and optimization of the mechanical, electrical, and chemical properties of CVD graphene.

MATERIALS AND METHODS

Preparation and transfer of graphene

Commercial (Graphenea) and in-house (45) CVD-grown single-layer graphene (Moorfield NanoCVD) was used in our experiments. An optimized wet transfer method was used to transfer single-layer CVD-grown graphene from the copper substrate to a SiO2 layer on a Si substrate (46). The thickness of the SiO2 layer was 125 nm. Before transferring the graphene, the SiO2 substrate surface was cleaned in piranha solution (a mixture of sulfuric acid and hydrogen peroxide with a volume ratio of 3:1) to remove possible organic contaminations. A poly(Bisphenol A carbonate) (PC) layer was spin-coated on the front side of the graphene/copper foils at 2000 rpm for 5 s and 2500 rpm for 30 s to deposit the polymer support layer (approximately 200 nm thick) during the graphene transfer process. Then, the samples were baked for 15 min at 45°C on a hot plate to evaporate the solvent. The carbon residues on the backside of the copper foil were removed using O2 plasma etching at low power (50 W). The copper foil was then placed on a surface of iron chloride (FeCl3) solution for wet etching of the copper, with the copper foil floating on the FeCl3 solution and the graphene side facing away from the liquid. After about 2 hours, the PC/graphene stack without copper residues floating on the FeCl3 solution was transferred with the aid of a Si chip onto the surface of deionized (DI) water, onto diluted HCl solution, and then finally back to DI water for cleaning and removing iron (III) residues and removing chloride residues, respectively. During this transfer process, it is important to keep the PC/graphene stack floating on the surface of the liquids and to keep the graphene side on top to prevent wetting of the PC covering the graphene by the etch solution. After the cleaning procedure, the PC/graphene stack was picked up with a SiO2-coated Si chip and dried.
on a hot plate at 45°C for 10 min to improve graphene adhesion to the substrate. After drying, the chips were put into chloroform for 24 hours to remove the PC, followed by an isopropanol dip for 5 min to remove chloroform residues. A nitrogen gun was used to gently dry the chips before baking them at 45°C for 10 min on a hot plate. The preparation of the double-layer graphene samples was based on an extension of the single-layer graphene transfer: Here, the PC/graphene stack floating on the DI water (as described for the single-layer transfer process) was transferred onto a second graphene film on copper foil and subsequently placed on a hot plate at 45°C to increase the adhesion between the two graphene layers. Carbon residues on the backside of the copper foil were removed using O₂ plasma. To remove the copper foil from the double-layer graphene/PC stack, we used a process identical to the case of single-layer graphene. Finally, the double-layer graphene/PC stack was transferred onto the SiO₂ substrate surface. All remaining steps were the same as in the single-layer graphene transfer process.

Experimental details of exposing the samples to VHF
The completed chips were mounted onto a custom-designed reaction cell with the graphene side facing toward the VHF chamber. VHF was generated passively from a 25% liquid HF solution placed in a small reservoir at the bottom of the reaction cell. The VHF penetrated the CVD graphene films at the grain boundaries and reacted with the SiO₂ surface. During the reaction, volatile SiF₄ was formed. The reaction of VHF with SiO₂ requires small amounts of H₂O to represent the surface. (42, 43). To obtain a microscopic water film on the surface without producing droplets and to accurately control the etching homogeneity, we gently heated the chips from the backside by a heater plate during the exposure to the VHF. In our experiments, the set temperature was 40°C. The expected reaction process was given by reactions (1) and (2) in the main text.

Characterization of the samples
The graphene films were inspected in situ using optical microscopy (Olympus BX 51 M) to obtain images with different magnifications displaying the morphologies of the graphene/SiO₂ surfaces before and after different times of VHF exposure. A scanning electron microscope (Gemini, Zeiss, Ultra 55) was used to investigate the surface morphology of the samples at different acceleration voltages to obtain high contrast images at different magnifications. EDX spectroscopy of graphene samples was also obtained with the same SEM tool to analyze trace elements on the graphene samples after VHF exposure. Raman spectroscopy was performed using an alpha300 R spectrometer (WITec) with a λ = 532 nm laser and a 100x objective. AFM images were obtained with a PSIA XE-100 (Park Systems) in tapping mode to analyze the morphologies and dimensions of the graphene grain boundaries after VHF exposure. A conventional probe station in connection with a SCS4200 parameter analyzer (Keithley) was used for four-probe measurements of the sheet resistances of the graphene samples before and after VHF exposure. LEEM/LEED characterization of CVD graphene on copper was done using a LEEM (FE-LEEM P90, Specs). The diffraction spots for dark-field imaging were selected by means of an aperture in the back focal plane of the objective lens.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/eaar5170/DC1

fig. S1. Initial formation of line defects after exposure to VHF for short time and formation of corrugations after exposure to VHF for a long time.

fig. S2. SiO₂ without graphene coverage after exposure to VHF.

fig. S3. Graphene placed on a 1.4-μm-thick SiO₂ layer and on the native SiO₂ layer of a Si substrate after exposure to VHF.

fig. S4. Sheet resistance of graphene placed on SiO₂ layers of different thicknesses after exposure to VHF.

fig. S5. SEM images of partially isolated single grains of CVD graphene with successively increasing magnification after exposure to VHF.

fig. S6. SEM images of double-layer graphene placed on a SiO₂ surface after exposure to VHF.

fig. S7. SEM images of graphene placed on a SiO₂ surface after exposure to 5% liquid HF.

table S1. Comparison of characterization methods of graphene grain boundaries in CVD graphene.

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Acknowledgments: We thank M. Otto for help with AFM characterizations. Funding: This work was supported by the European Research Council through the Starting Grants M&M (277879) and IntegraDe (307311), the Swedish Research Council (GRMS, 2015-05112), the China Scholarship Council, the German Federal Ministry for Education and Research (NanoGraM, BMF, 03XP0006C), and the German Research Foundation (DFG; LE 2440/1-2). The Chemnitz group acknowledges support by the German Research Council (DFG) through the Priority Program SPP 1459 Graphene. Author contributions: X.F., F.N., and M.C.L. conceived and designed the experiments. X.F., performed the experiments and optical, electrical, and SEM characterizations and wrote the manuscript. S.W. performed the AFM characterization. S.W. and S.K. performed the Raman spectroscopy characterization. P.S., F.S., and T.S. performed LEEM and LEED characterization. T.H. contributed to the analysis of the chemical reactions. F.N. and M.C.L. provided guidance in all the experiments and manuscript writing. All authors analyzed and discussed the results and commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 17 November 2017
Accepted 12 April 2018
Published 25 May 2018
10.1126/sciadv.aar5170

Direct observation of grain boundaries in graphene through vapor hydrofluoric acid (VHF) exposure
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DOI: 10.1126/sciadv.aar5170

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