Epitaxial Hexagonal Boron Nitride for Hydrogen Generation by Radiolysis of Interfacial Water

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ABSTRACT: Hydrogen is an important building block in global strategies toward a future green energy system. To make this transition possible, intense scientific efforts are needed, also in the field of materials science. Two-dimensional crystals, such as hexagonal boron nitride (hBN), are very promising in this regard, as it has been demonstrated that micrometer-sized flakes are excellent barriers to molecular hydrogen. However, it remains an open question whether large-area layers fabricated by industrially relevant methods preserve such promising properties. In this work, we show that electron-beam-induced splitting of water creates hBN bubbles that effectively store molecular hydrogen for weeks and under extreme mechanical deformation. We demonstrate that epitaxial hBN allows direct visualization and monitoring of the process of hydrogen generation by radiolysis of interfacial water. Our findings show that hBN is not only a potential candidate for hydrogen storage but also holds promise for the development of unconventional hydrogen production schemes.

KEYWORDS: bubbles, hydrogen production, hydrogen storage, Raman spectroscopy, hydrogen barrier, deuterium

Although hydrogen is the most abundant element in the solar system, its production and storage constitute a major scientific challenge that hinders its widespread application: for example, as a fuel or feedstock.1,2 It has been experimentally shown that hexagonal boron nitride (hBN)3 holds great prospects for hydrogen applications because it is an excellent proton conductor,4,5 a molecular hydrogen barrier,6,7 and an electrical insulator8 that can withstand high temperatures and harsh environments.9,10 Moreover, hBN shows exceptional mechanical properties,11 which are currently being explored in fields like flexible electronics.12 The main challenge is to preserve the above properties while scaling from submillimeter-sized mechanically exfoliated samples to thin films with a large area.13 In this work, we grow hexagonal boron nitride by molecular vapor phase epitaxy (MOVPE) on 2 in. sapphire substrates.14−17 For such hBN epilayers, we observed the formation of bubbles upon electron beam irradiation under vacuum with a scanning electron microscope (SEM). A typical example of bubble formation is shown in Figure 1c. The four images that were taken at different times (the whole sequence took about 20 s) show that first some tiny bubbles appear within the field of view and then gradually grow in diameter and height as the exposure continues. Eventually, bubbles may combine to form larger bubbles until all bubbles merge into a single large bubble that will rise roughly to the size of the exposed area (Videos 1−2 of the whole evolution of bubble formation are available in the Supporting Information). An example of bubble formation can be seen in the optical microscope image (Figure 1d). Here, only the label “hBN” (marked by a dark shadow) was exposed to electron beam irradiation. One can clearly see that bubbles only form in or at the borders of the exposed areas and not on the whole sample. Interestingly, these bubbles remained stable even after the sample was removed from the high vacuum in the SEM and exposed to the ambient environment. As can be seen in the AFM image in Figure 1b, hBN grown by MOVPE on sapphire shows many wrinkles. This behavior has already been reported16,18,19 and can be ascribed to differences in the thermal expansion coefficients of hBN and sapphire, as shown schematically in Figure 1a.

Since the hBN layer is only weakly attached to the substrate, the strain induced during the cooling process leads to this typical wrinkle pattern. Bubble formation is one way to relax the strained wrinkle pattern locally, as can be seen in Figure 1e. Once the layer detaches, this strain redistribution stabilizes the
bubble. Although it is clear that compressive strain favors bubble formation, the actual mechanism that leads to local delamination has yet to be identified. Important in this regard is that the bubbles form only in the irradiated areas, which means that they are a direct result of the electron-beam exposure. Because both the sapphire substrate and the hBN epilayer are insulating materials, electrostatic charging could be responsible. Indeed, charging effects are observed during SEM characterization and hinder high-resolution imaging. Another possible mechanism could be a chemical reaction involving gas evolution triggered by the electron beam. To shed more light on the actual mechanism, micro-Raman spectroscopy mapping was performed.

Figure 1. Bubble formation mechanism. (a) Schematic illustration of the bubble formation. hBN is grown by MOVPE at temperatures above 1000 °C. After the growth the sample is cooled to room temperature, which leads to the formation of hBN wrinkles. The sample is removed from the reactor and exposed to ambient conditions. Electron beam exposure in an SEM leads to bubble formation. (b) AFM image of a typical wrinkle pattern. (c) Evolution of the SEM image as a function of exposure time. The acceleration voltage was 5 kV and the current was 1.4 nA. The whole image sequence took about 20 s. The white scale bars correspond to a length of 5 μm. (d) Optical microscope image of bubbles exposed in the shape of an "hBN" label. The reddish dark shadow marks areas that were exposed by the electron beam. The white scale bar corresponds to a length of 20 μm. The red square indicates the region measured by AFM in (e). The AFM image shows that the wrinkle pattern vanishes on the bubbles due to strain relaxation, while it remains clearly visible elsewhere.

Figure 2. Evidence of molecular hydrogen in Raman spectroscopy. (a) Raman line scan across a hydrogen-filled bubble. It can be clearly seen that two lines are present only on the bubble. These lines correspond to the lines of molecular hydrogen S(0) at 354 cm⁻¹ and S(1) at 587 cm⁻¹. The Raman spectra are shifted vertically for clarity. (b) Optical micrograph image of the studied bubble showing the laser spot (532 nm). The dashed line indicates the direction of the line scan. (c) Additional rovibrational lines measured on the bubble not shown in the line scan. It was possible to identify the first four lines S(0)–S(3) of the (0−0) transitions and line Q(1) of the (1−0) transitions.
therefore, one could expect that back diffusion of hydrogen into the_interfacial_water layer will be limited by the high energy barrier.

**Figure 2a** shows the results of a line scan (step 2 μm) across a bubble as indicated in **Figure 2b**. The subsequent spectra are shifted vertically for the sake of clarity. Astonishingly, some very narrow Raman bands were only present when the laser was focused on the bubble. Two of these bands are marked in **Figure 2a** by vertical dashed lines at 354 and 587 cm⁻¹. **Figure 2c** presents all five peaks that could be clearly observed and that could be recorded only when the laser spot was on the bubble. The observed peaks can be ascribed to S(0)–S(3) of the (0–0) transitions and the Q(1) line of the (1–0) transitions of molecular hydrogen. The observed presence of hydrogen inside the bubbles clearly points toward a chemical reaction triggered by the electron beam as a mechanism for bubble formation.

There are two possibilities to explain the source of hydrogen that leads to the formation of bubbles. First, the hydrogen gas is the result of the hydrogen accumulated in the layer during growth. Hydrogen is available in large amounts both in the precursor gases and in the carrier gas and can, for example, decorate defects or be stored between layers. Second, the hydrogen source is introduced after growth, for example, by intercalation of water. To distinguish between these two possibilities, we placed a hBN/sapphire sample directly after growth inside a sealed container with heavy water. The sample was not in direct contact with the heavy water but was mounted upside down at the top of the container. The container was kept closed for more than 20 days at room temperature to allow a possible intercalation of heavy water.

After this period, the sample was removed and directly mounted inside the SEM for electron beam irradiation. **Figure 3a** shows a schematic drawing of this experiment. Similarly to the results shown in **Figure 1**, bubbles formed under irradiation. The samples were removed from the SEM and measured by micro-Raman spectroscopy. Raman bands associated with dimolecular hydrogen were identified, in agreement with **Figure 2**. However, in addition we observed novel bands at 267 and 616 cm⁻¹ that can be ascribed to the rovibrational lines S(0) and S(2) of hydrogen deuteride (HD) (**Figure 3b**). The S(1) line at 443 cm⁻¹ also becomes visible after subtracting the Raman signal from the sapphire (see **Figure 3c**). The presence of deuterium clearly shows that intercalation occurs and that at least part of the hydrogen in the bubbles is connected to the water vapor introduced after growth, as was schematically shown in **Figure 1a**. This finding allows us to conclude that bubbles are formed as a result of the dissociation of water by electron irradiation (radiolysis). Such a radiolytic splitting of water has been already observed in special liquid cells allowing for direct irradiation of water in an electron microscope. The first studies on the radiolysis of water date back to the beginning of the 20th century. The processes involved have been extensively studied and are of great importance: for example, for the safety and construction of nuclear plants. More recent works show that the hydrogen generation yield by radiolysis of water can be greatly enhanced for certain wide-band-gap semiconductors and for water confined in nanostructures. Such enhancements would be needed to revisit the idea of hydrogen production via radiolysis of water using spent nuclear fuel. More work is needed to determine the hydrogen generation yield of nanoconfined water in our hBN layers for different sources of ionizing radiation, but it is clear that the strained hBN/sapphire material system is exceptional because the formation of hBN bubbles allows for direct observation of the hydrogen gas production.

To explore storage capabilities, we monitored the Raman spectrum of H₂ over time. We found that H₂ can still be measured 4 weeks after exposure for a 40 nm thick layer (**Figure 4a**). After this time period, the bubble did not change visibly under the microscope, but the H₂ signal disappeared. The H₂ generated after radiolysis, all other stable molecules (mostly H₂O₂), and the remaining interfacial water are confined to the bubble. Therefore, one could expect that back diffusion of hydrogen into the_interfacial_water layer will be limited by the high energy barrier. **Figure 4b** shows a schematic drawing of this experiment, which is essentially the same as **Figure 3a**. The bubble was kept in a sealed container filled with heavy water for 23 days. Afterward the sample was directly mounted in the SEM and exposed by e-beam irradiation to form bubbles as shown in (**Figure 4b**). The spectrum next to the bubble shows only Raman bands related to sapphire (the Raman band of hBN is at a higher energy; see the Supporting Information). For the measurement on the bubble not only a signal related to molecular hydrogen but also a signal related to hydrogen deuteride (HD) can be observed. After subtracting the sapphire signal, three peaks (S(0), S(1), and S(2)) related to HD can be clearly observed.

**Figure 3.** Origin of the hydrogen. (a) The sample was mounted upside down in a container filled with heavy water (D₂O) for 23 days. Afterward the sample was directly mounted in the SEM and exposed by e-beam irradiation to form bubbles as shown in (**Figure 4b**). (b) Raman spectra of two typical points on (next to) the bubble are shown as red (green) curves. The spectrum next to the bubble shows only Raman bands related to sapphire (the Raman band of hBN is at a higher energy; see the Supporting Information). For the measurement on the bubble not only a signal related to molecular hydrogen but also a signal related to hydrogen deuteride (HD) can be observed. (c) After subtracting the sapphire signal, three peaks (S(0), S(1), and S(2)) related to HD can be clearly observed.
Raman measurements were performed. Molecular hydrogen was still present after 551 cycles between 100 and 400 mbar (see Video 3 in the Supporting Information for a video of a typical cycle). After certain numbers of pressure cycles, microscope images of a large bubble for different ambient pressures. The bubble was inflated and deflated by automatically cycling the pressure. Bubble after 1 month under ambient conditions. The Raman spectrum of a bare sapphire substrate is shown for comparison. (b) Optical microscopy after electron beam exposure and after 4 weeks. The Raman lines did not decrease in intensity. This means that the hydrogen is still confined in the bubble. A similar suppression of back reactions shows the presence of molecular hydrogen. Experiments with hBN bubbles are formed on 2 in. sapphire substrates is a prospective material for lightweight storage tanks. In summary, we show that epitaxial hBN has the potential to be applied in future field of application, but the presented results already indicate that epitaxial hBN has the potential to be applied in future innovative hydrogen generation and storage schemes.

METHODS

Boron Nitride Growth. The boron nitride layers were grown on 2 in. sapphire substrates (c-plane) by metal–organic vapor-phase epitaxy (MOVPE) using an Aixtron CCS 3 × 2 in. reactor equipped with an ARGUS Thermal Mapping System to directly control the substrate temperature. Growth precursors were triethylborane (TEB) and ammonia. Hydrogen was used as the carrier gas. The layers were grown by pulsed growth and two-stage epitaxy at temperatures typically between 1260 and 1300 °C.

Characterization. Micro-Raman spectra were recorded using a Renishaw inVia Raman setup equipped with a 532 nm continuous wave laser excitation source and a 100X objective. The spot size was about 1 μm with a laser power of 30 mW. The system has an automated xyz stage with a resolution of 100 nm. SEM imaging and e-beam exposure were performed on a FEI Helios 600 Dual Beam system, equipped with a Raith Elphy electron lithography setup. AFM images were acquired with a Bruker Dimension Icon microscope/Nanoscope VI controller in a PeakForce mode. Bruker ScanAsyst Air probes were used for imaging.

ASSOCIATED CONTENT

Data Availability Statement
The data that support the findings of this study are available online: 10.18150/BSUHH4.

Supporting Information
The Supporting Information contains The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c04434.
Additional Raman and X-ray diffraction measurements (PDF)

Bubble formation in situ in a scanning electron microscope (AVI)

Bubble formation in situ in a scanning electron microscope (AVI)

Pumping cycles (bubble deformation) recorded in an optical microscope (AVI)

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Notes

The authors declare no competing financial interest.

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