High-Vacuum Chemical Vapor Deposition of Monolayer Hexagonal Boron Nitride on Ge(001) from Borazine

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Hexagonal boron nitride (h-BN) is a promising material for next-generation electronics due to its unique optoelectronic and electronic properties. While the synthesis of h-BN on metallic substrates has been studied extensively, h-BN synthesis on CMOS-compatible substrates like Ge has not. Here, we report the growth of h-BN on Ge(001) from borazine via high-vacuum chemical vapor deposition. We find that the sublimation of Ge under high vacuum inhibits h-BN growth. To overcome this challenge, we place two Ge substrates face-to-face and achieve the growth of aligned h-BN islands and monolayer h-BN films.

Introduction

Hexagonal boron nitride (h-BN) has played significant roles in enhancing the optoelectronic and electronic properties of a wide variety of two-dimensional materials. These include reducing charge scattering in field-effect transistors(1, 2), increasing exciton emission efficiency in valleytronics(3, 4), controlling interlayer excitons(5, 6), acting as a passivation layer(7, 8), and serving as a tunneling barrier(9). While the bottom-up synthesis of h-BN films on metallic substrates has been studied extensively(10–16), h-BN synthesis on semiconducting, CMOS-compatible substrates has not. There exist a few instances of h-BN grown on Ge from the solid precursor, ammonia borane.(17, 18) In this work, we choose liquid borazine as the h-BN precursor over ammonia borane due to the complexity of ammonia borane decomposition, which involves the release of at least eight chemical species(19), the possibility of condensation of ammonia borane vapor within the tube furnace and pumps, and the relatively high vapor pressure of borazine(*19*). Monolayer h-BN has been grown from borazine on a wide variety of metallic substrates via high or ultra-high vacuum deposition techniques.(*10–16*) However, while multilayer h-BN has been grown on Ge from borazine, single layer control has not yet been achieved (*20*). Here, we present the first synthesis of h-BN islands and a monolayer h-BN film on Ge(001) via high-vacuum chemical vapor deposition (CVD) of borazine.

Results and Discussion

To grow h-BN, 1 cm squares of Ge wafer are loaded into a tubular CVD reactor (with an inner diameter of 34 mm), annealed in a 2:1 mixture of Ar:H_2 at 910 °C for 1 hour to remove their native oxide and hydrocarbon adsorbates, and cooled. Then, the reactor is pumped down to below 2×10^{-6} Torr. During this time, the h-BN precursor, borazine

(from Gelest, Inc.) is purified via freeze-pump-thaw cycles with liquid nitrogen. To initiate h-BN growth, a box furnace held at 870-900 °C is slid over the samples and borazine is leaked into the system until the system pressure increases by 5×10^{-6} Torr. We find that when the face of the Ge substrate is exposed to the vacuum, h-BN growth is not observed. We attribute this to Ge sublimation, which occurs easily under high vacuum at temperatures near the Ge melting point and is evidenced by the presence of etch pits on the Ge surface (Figure 1a). However, h-BN growth is observed when the substrate is loaded face-to-face with another piece of Ge wafer (Figure 1b). We attribute this to the suppression of Ge sublimation, which may arise from the build-up of vapor pressure in the narrow gap between pieces of Ge wafer that are not perfectly flat. Using a face-to-face substrate configuration, growth temperature of 880 °C, and growth time of 36 min, we grow h-BN islands that are highly aligned and triangular, with side lengths of approximately 250 nm.

We also find that the h-BN island alignment and morphology are highly dependent on growth temperature. At 900 and 890 °C, the h-BN islands have rough edges and no orientational order (Figure 2a-b). At 880 °C, the h-BN islands are triangular with orientations that can be categorized into two groups of anti-oriented domains along the Ge<110> directions, owing to the four-fold symmetry of the Ge(001) surface (Figure 2c). Upon decreasing the temperature further to 870 °C, the h-BN islands are still aligned but have a less regular shape, i.e., jagged edges and rounded corners, possibly due to reduced thermal energy for adatom diffusion (Figure 2d).

When the reaction time is increased to 90 min, the h-BN domains coalesce into a continuous film. The lack of contrast in SEM images shows that the h-BN films are uniform (Figure 3a). For further characterization, h-BN films are wet-transferred to 90 nm SiO_2/Si. First, a thick, supportive layer of poly(methyl methacrylate) (PMMA) is spin-coated on top of the h-BN film. PMMA residue on the bottom of the Ge substrate is removed using toluene and reactive-ion etching in O_2. The substrate is then suspended in a 3:1:1 H_2O:HF:H_2O_2 solution until all of the Ge has etched away and the film can be scooped onto the target substrate. Finally, the sample is soaked in acetone and then annealed under high vacuum at 400 °C to remove PMMA. The films are characterized via Raman spectroscopy with a laser wavelength of 405 nm. The Raman spectrum shows a peak at 1370 cm^{-1} with a FWHM of 30.7 cm^{-1} (Figure 3b), confirming the presence of an h-BN layer that is a monolayer thick.

Conclusions

In this work, we demonstrate the growth of monolayer h-BN on Ge(001) from borazine for the first time. We find that suppression of Ge sublimation under high-vacuum is paramount for h-BN growth and can be achieved by placing the Ge substrates face-to-face. In the future, it may be possible to improve the scalability of this process by instead suppressing Ge sublimation by co-dosing with borazine and germane, a vapor-phase Ge precursor.

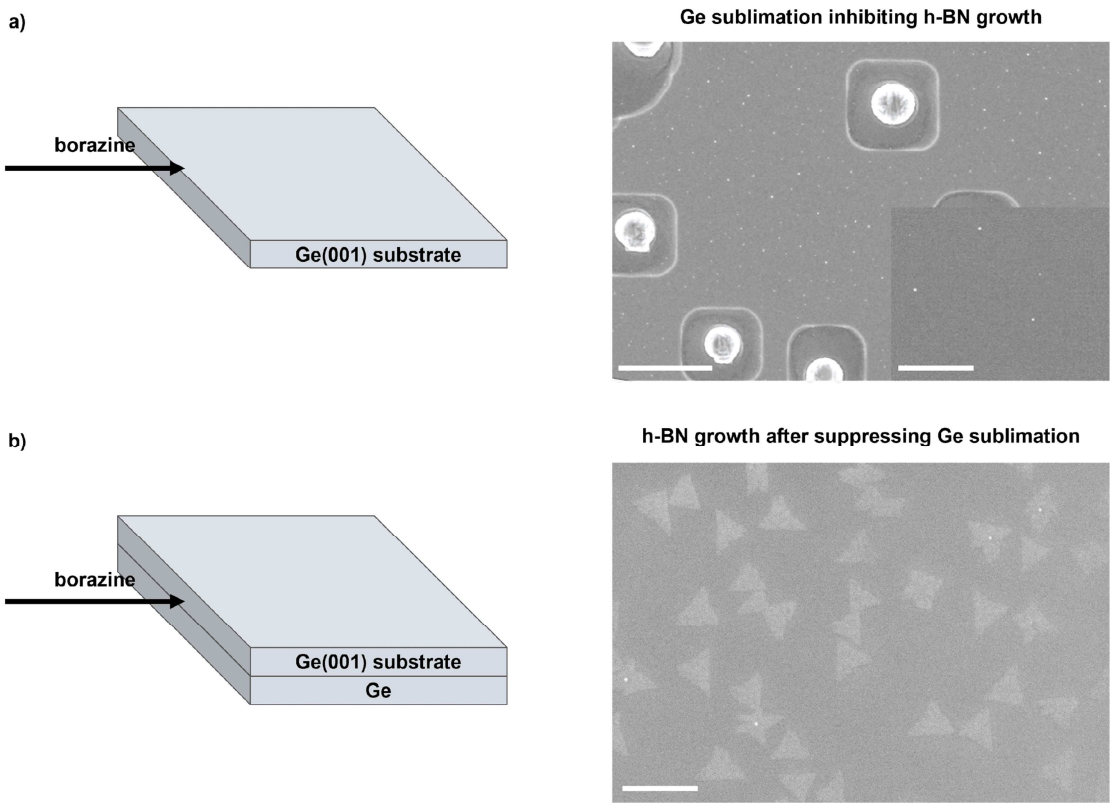

Figure 1. a) Substrate schematic and SEM image depicting etch pits and lack of h-BN growth when the substrate face is exposed to vacuum. Scale bar is 4 μm (inset scale bar is 400 nm). b) Substrate schematic and SEM image depicting h-BN triangles when the substrate is placed face-to-face with another piece of Ge wafer. Scale bar is 400 nm.

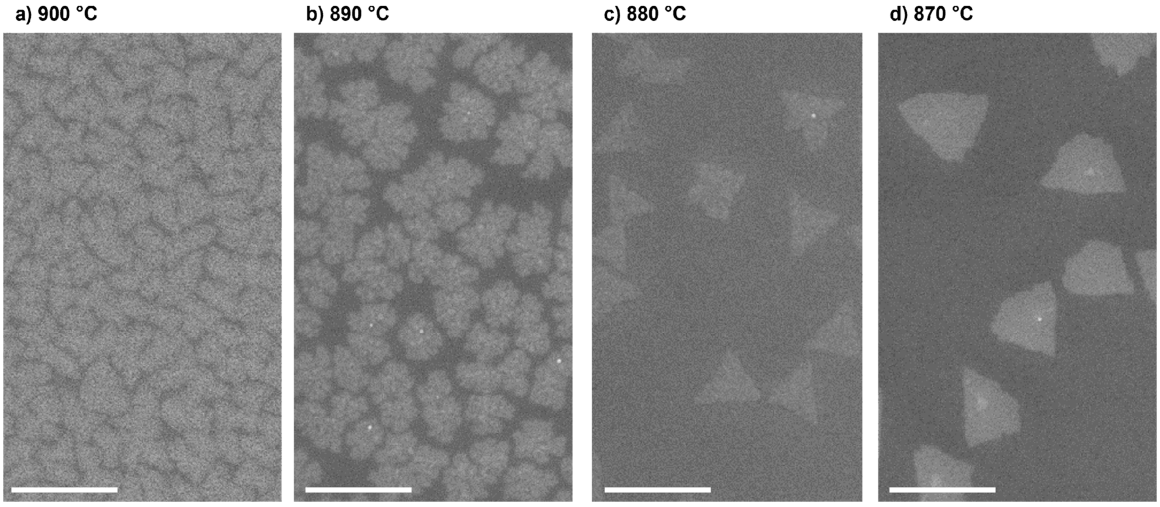

Figure 2. SEM images of h-BN islands grown with a face-to-face substrate configuration at a) 870, b) 880, c) 890, and d) 900 °C. Scale bars are 400 nm.

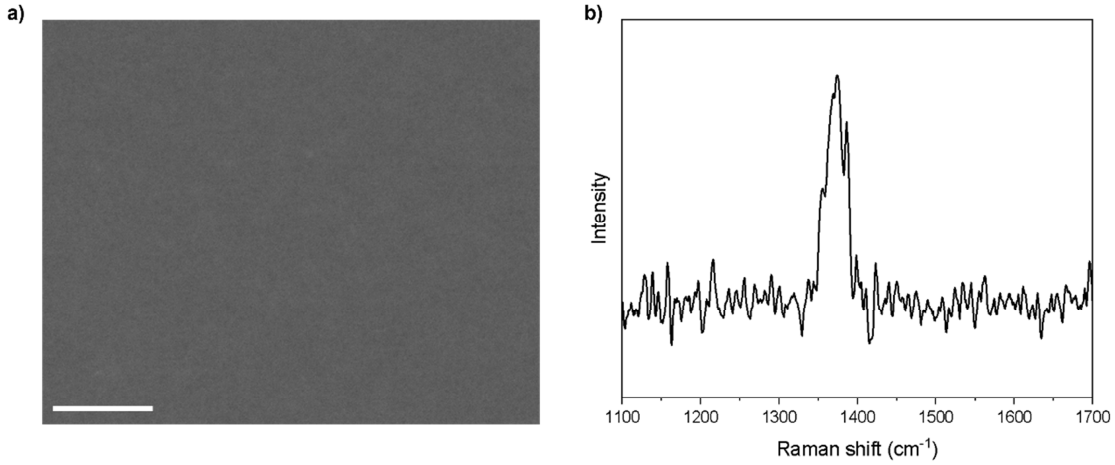

Figure 3. a) SEM image of monolayer h-BN. Scale bar is 500 nm. b) Raman spectrum of an h-BN film transferred to SiO_2/Si.

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